A graphical method for calculating ion exchange columns

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Summary—The equilibrium conditions of a system, " electrolyte solution – cation exchanger," can be represented in two-dimensional diagrams. These diagrams show a strong resemblance to those used in the graphical calculation methods for distilling columns.

The points of similarity between the procedures for distillation and ion exchange processes are discussed. This analogy is not very marked, because the ion exchange process is discontinuous. Yet it is possible to develop graphical methods of calculation for ion exchange analogous to those of PONCHON & SAVARIT and McCABE & THIELE for distillation. This method has been worked out for a simple percolation column. The method given includes all the essential quantities and can easily be developed for application to more complicated problems.

Résumé—L'auteur étudie la représentation par des diagrammes rectangulaires des conditions d'équilibre entre une solution d'electrolytes et un échangeur de cations. Ces diagrammes sont tout à fait analogues aux diagrammes classiques de distillation.

L'auteur discute les relations entre les divers modes de distillation et le processus d'échange d'ions, relations moins étroites puisque ce dernier procédé est discontinu. Les méthodes graphiques pour l'étude des échanges d'ions sont absolument identiques aux methodes de PONCHON et SAVARIT, ou McCABE et THIELE. La methode de calcul étudiée en détail pour une colonne à percolation simple peut être étendue très simplement à des cas plus complexes.

I. INTRODUCTION

In recent years much thought has been given to the mathematical description of the performance of a cation exchange column. The requirements of mass conservation form the starting point. To integrate the differential equation of the conservation condition for the non-stationary state in a cross-section of the filter bed, an expression for the relation between the ion-concentration in the solution and in the exchanger must be known. This relation may be expressed by the distribution equation for equilibrium conditions or by the differential equation for the rate process for one general class of rate laws.

DE VAULT [1] gave a solution by using the equation of the distribution equilibrium, and assumed that equilibrium is reached throughout the column. BOYD, MYERS and ADAMSON [2] used a first order differential rate equation for mass transfer, assuming that the rate of diffusion through the liquid film enveloping the solid particle governs the rate of the ion exchange process. THOMAS [3] made use of the equation for the rate of opposing second order and first order reactions. Such a rate law is to be expected if the exchange processes are slow compared with any diffusion process in the solution or in the solid particle.

With these mathematical considerations it is inevitable to include the mechanism of the exchange process in the calculations. However, one cannot include more than one mechanism so that the picture obtained has only a very limited validity. This lack called for a method of calculation which was independent of the mechanisms of mass transfer and ion exchange.

For the distillation process such a method was developed by McCABE and THIELE and by

PONCHON and SAVARIT. SAAL and VAN DIJCK [4] have shown that completely analogous calculations can be applied to the extraction process. DONKER [5] has pointed out that this analogy can be extended to include the process of ion exchange.

These calculations are based on the fact that it is always possible to represent the equilibrium conditions of the system vapour-liquid or extract-raffinate in a two-dimensional diagram. The quantities on the axes of the diagrams are variables from the equation of the material balance. This makes it possible to represent in the diagram, besides the equilibrium conditions, also the operation of the column.

The equilibrium conditions of the system, "electrolyte solution – cation exchanger," can also be plotted in two-dimensional diagrams. These are analogous to the enthalpy-composition diagram and to the vapour-liquid composition diagram of the distillation process. The derivation of these diagrams will not be dealt with in further detail here.

If distillation, extraction and ion exchange processes can be treated in a similar way, the conditions necessary to optimum methods for distillation must, properly transformed, imply those for ion exchange. Introduction of this method of calculation for processes in a fixed filter bed has the additional advantage of contributing towards classification of the ion exchange process as one of the " Unit Operations."

We have limited ourselves to a system of an electrolyte solution containing two salts with the same anion and different cations, and a cation exchanger containing the two cations. These two cations have been considered here as the two components of the system so as to obtain a simple representation of facts.

II. PROCESSES IN ONE EQUILIBRIUM STAGE (SHAKING IN BATCHES)

The simplest form of the distillation process is the fractional evaporation in one equilibrium stage (Fig. 1, I). An amount of heat is applied to a binary liquid mixture so as to produce partial evaporation. This gives rise to formation of two phases ; the vapour phase and the liquid phase are in equilibrium and have different compositions. Now, if the two phases are removed separately, partial separation of the components will result. This process can be simply represented in an enthalpy-composition diagram (see DODGE [6]).
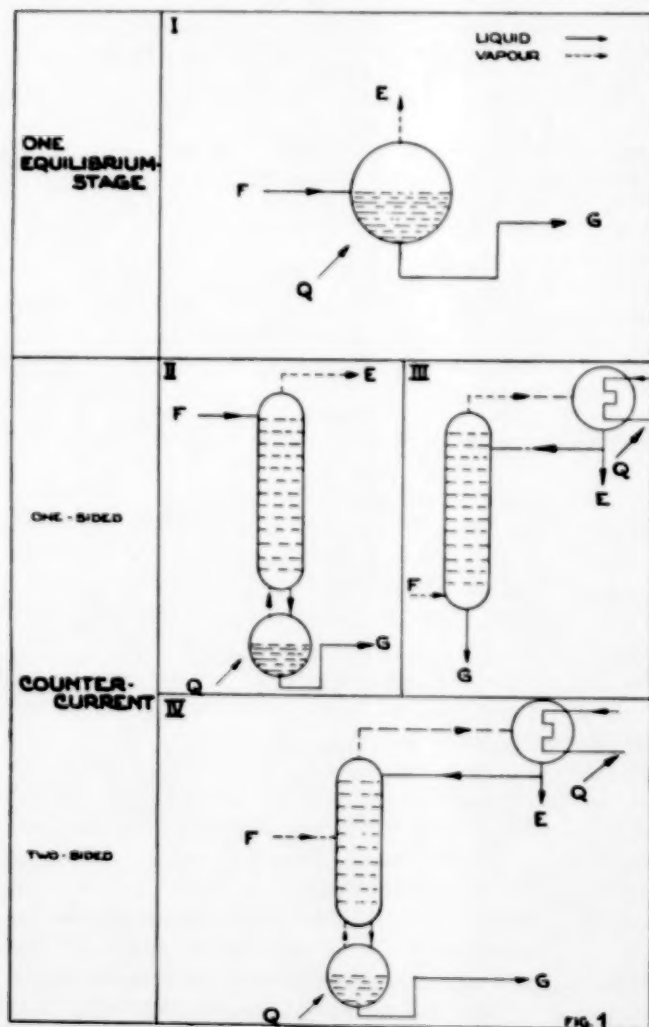

Fig. 1

In the application of ion exchangers this method is analogous to batchwise shaking of an electrolyte solution containing the salts AZ and BZ, with a cation exchanger ($AR + BR$). After some time the exchanger and the electrolyte solution will be in equilibrium. Separation of exchanger and electrolyte solution will result in a partial separation of the cations A^+ and B^+.

This process can be represented graphically in the equilibrium diagram (Fig. 2). On the
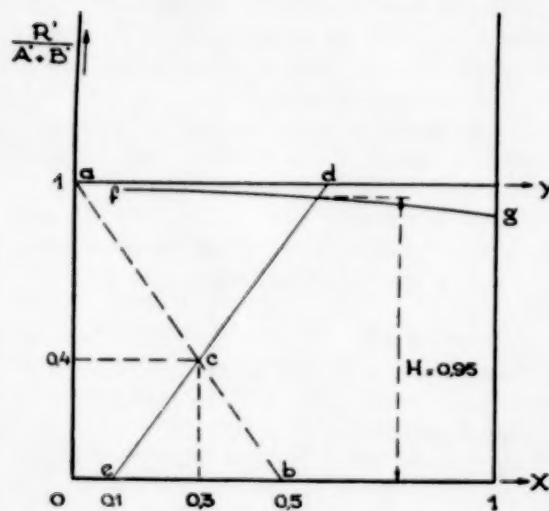

Fig. 2.

Gram equivalents of B^+ per gram equivalent of $(A^+ + B^+)$

abscissa has been plotted the number of gram equivalents of B^+ per gram equivalent of $(A^+ + B^+)$, indicated by X for the electrolyte solution and by Y for the exchanger. Accordingly, each point of the diagram refers to one gram equivalent of $(A^+ + B^+)$. On the ordinate has been plotted the number of gram equivalents of R' per gram equivalent of $(A^+ + B^+)$; $\frac{R'}{A^+ + B^+}$.

Assume an ion exchanger has been completely saturated with the cation A^+ and then thoroughly eluted. This exchanger will not contain any ions other than the cations A^+ and the active groups R' which are present in equivalent quantities. The ratio $\frac{R'}{A^+ + B^+}$ is therefore equal to unity and the ratio $\frac{B^+}{A^+ + B^+} = Y$ is equal to

zero. The exchanger can therefore be represented in the diagram by point a with the co-ordinates $Y = 0$ and $\frac{R'}{A^+ + B^+} = 1$.

Assume that the equivalent fraction of B^+ in the electrolyte solution is $X = 0.5$. This solution does not contain any active groups R' of the exchanger, so the ratio $\frac{R'}{A^+ + B^+}$ is equal to zero. The electrolyte solution can therefore be represented by point b with co-ordinates $X = 0.5$ and $\frac{R'}{A^+ + B^+} = 0$.

Now, if we contact a volume of the electrolyte solution with a quantity of exchanger, we obtain a heterogeneous mixture or " overall phase." The overall composition of this mixture is represented by a point c on the line a-b. The ordinate is determined by the number of gram equivalents of R' per gram equivalent of $(A^+ + B^+)$ in the overall phase.

After equilibrium has been reached the compositions of the exchanger and the electrolyte solution are represented by the ends e and d of the nodal line through c.

If the exchanger is separated from the electrolyte solution, a certain amount of the latter adheres to the exchanger. The exchanger together with the adhering solution forms in turn an " overall phase." Therefore, in actual practice the ion exchanger is always present as an " overall phase " as mentioned above. For the sake of simplicity we will define this " overall phase " as the exchanger.

Besides RA and RB, the exchanger contains an amount of electrolyte solution, hence an amount of AZ and BZ; the ratio $\frac{R'}{A^+ + B^+} = H$ will be smaller than unity. Line f-g, representing the exchanger in the diagram therefore lies below the line $\frac{R'}{A^+ + B^+} = 1$. The equivalent fraction of B^+ in the adhering solution is assumed to be the same as in the bulk of the electrolyte solution so the point of intersection of the nodal line through c and the line f-g represents the exchanger.

Example :

A volume of electrolyte solution containing 3 gram equivalents of $(A^+ + B^+)$, equivalent fraction of B^+ equal to $X = 0.5$, is shaken with a quantity of completely eluted exchanger RA. This quantity represents 2 gram equivalents of R', hence also 2 gram equivalents of A^+. The system electrolyte solution plus exchanger can be represented by a point e with ordinate $\frac{R'}{A^+ + B^+} = \frac{2}{5} = 0.4$ and abscissa $\frac{B^+}{A^+ + B^+} = \frac{1.5}{5} = 0.3$.

After the equilibrium has been attained the electrolyte solution is filtered. Suppose that by analysis of the electrolyte solution we have found 2.9 gram equivalents of $(A^+ + B^+)$ and 0.29 gram equivalent of B^+. The equivalent fraction of B^+ is equal to $X = 0.1$.

The exchanger is now represented by the point of intersection of a straight line through e and the point $X = 0.1$; $\frac{R'}{A^+ + B^+} = 0$, the nodal line, and the line f-g. The co-ordinates of this point can be calculated :

$$H = \frac{R'}{A^+ + B^+} = \frac{2}{2.1} = 0.95$$

$$Y = \frac{B^+}{A^+ + B^+} = \frac{1.21}{2.1} = 0.58.$$

If the equilibrium diagram, i.e. the positions of both the nodal lines and the exchanger line under the conditions considered are known, the effect of shaking can be determined in advance. On the other hand, the positions of the nodal lines and of the exchanger line can be determined by analysis of the exchanger and the electrolyte solution before and after shaking.

III. PROCESSES BASED ON THE COUNTER-CURRENT PRINCIPLE.

Comparison of the continuous procedures used in distillation with those of the ion exchange process gives rise to some difficulties because the procedures used for the latter are discontinuous.

A continuous process is constant with respect to time and its consideration is invariably based on a steady state. It is therefore necessary to design a model of the ion exchange process which meets this requirement.

In an exchange column of infinite length, through which an electrolyte solution is percolated, there is an exhausted part, a part where the exchange is taking place (i.e. the so-called transition part) and a part containing the fresh exchanger. A section of the transition part of the column between two horizontal cross-sections at some distance from each other, may serve as a model for our purpose. This section moves at such a speed that it may be considered as being in a steady state.

This model is approximated in such cases where the height of the transition part is small with respect to the length of the column. If it is not small with respect to the length of the column, an average stationary state can be reached by means of a number of exchange filters placed in series.

Every time the filter on the influent side of the series is exhausted it is put out of use and separately regenerated. At the same time a freshly regenerated filter is included in the series at the effluent side. The total number of filters in the series remains constant.

Thus we have outlined a model of an ion exchange column for continuous operation in which the electrolyte solution and the exchanger are in countercurrent.

(A) Distillation

i. Rectifying evaporation (Fig. 1, II). A binary mixture is introduced as a liquid at the top of a column. This liquid is evaporated at the bottom, except for a part that is drained at the bottom and which contains only a very small quantity of the most volatile component B. The vapour leaving the column at the top contains, besides component B, a considerable quantity of component A.

ii. Rectifying condensation, (Fig. 1, III). The mixture is introduced as vapour at the bottom of the column. The vapour leaving the column at the top is completely condensed. The condensate flows down the column as reflux except for a part which is drawn off at the top. In this

way the most volatile component B can be obtained in a fairly pure state. The liquid leaving the column at the bottom contains, besides component A, a considerable amount of component B.

iii. Complete rectification, (*Fig.* 1, *IV*). The figure shows clearly how the principle of complete rectification can be realized by superposition of columns 1 and 2. The more volatile component B is obtained as top product in an almost pure state. The less volatile component A is drawn off as bottom product, also in an almost pure state. In this way a binary mixture can be split into its components.

(B) Ion exchange

By simple percolation of an electrolyte solution with salts AZ and BZ through a filter with a cation exchanger the cation B^+ can be almost completely removed from the solution, the ion exchanger being only partly saturated with cation B^+. This procedure is analogous to rectifying evaporation.

On regeneration of the filter with an electrolyte solution containing only AZ, we can, by simple percolation, obtain an ion exchanger that is almost completely saturated with cation A^+, while the liquid contains, besides B^+, still a considerable amount of A^+. This procedure is analogous to rectifying condensation.

The analogy is not complete, however. In rectifying evaporation the bottom product is in equilibrium with the vapour entering at the bottom of the column. In rectifying condensation the vapour leaving the column and the liquid flowing back have the same composition, the vapour phase being totally condensed. In the ion exchange process it is, naturally not possible to convert the electrolyte into the exchanger, or conversely.

It might be useful to find out what should happen in a " condenser " for the ion exchange process in order to complete the analogy with the distillation process. In this hypothetical condenser the exchanger $(RA + RB)$ will be contacted with a solution of a salt CZ. The salt CZ will, by definition, be chosen such that cation C^+ completely displaces cations A^+ and

B^+. The quantity of CZ will be so adjusted that it is equivalent to the quantity of A^+ and B^+ in the exchanger. The exchanger will leave the condenser in the form of RC and the electrolyte solution CZ will have been converted into the solution $(AZ + BZ)$ of the same normality. Part of this solution is withdrawn as top product ; the rest is passed back into the column as reflux. This is represented schematically in Fig. 3.
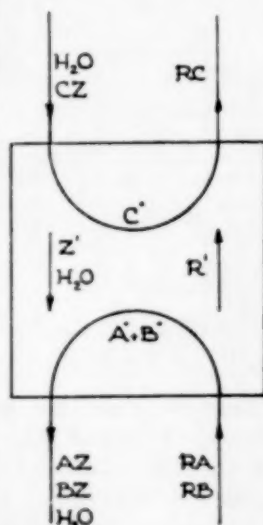
Similarly, a diagram for the operation of an evaporator for the ion exchange process can be drawn up.

Fig. 3.

In the calculation methods for the distillation process use is made of the relation between the compositions of the vapour and liquid phases at the top and at the bottom of the column respectively. In the ion exchange process there will, in general, be no such relation, but this does not hamper the development of methods of calculation.

In the ion exchange process it is also possible to apply the principle of complete rectification by building up the column of two parts. Half-way up this column the electrolyte solution is fed in. The lower part now simply works as a percolating column. At the bottom the exchanger, which is entirely saturated with cation A^+, enters the column. Half-way up the column this exchanger is only partly saturated with cation B^+. In the upper part of the column the exchanger is now eluted by means of an artificial reflux of an electrolyte solution containing BZ. Thus we recover from the bottom of the column an electrolyte solution containing almost exclusively cation A^+ and from the top of the column an exchanger almost entirely saturated with cation B^+.

IV. Methods of Calculation.

A column for continuous percolation is represented schematically in Fig. 4. The electrolyte solution contains the two cations A^+ and B^+. In this column cation B^+ is almost completely removed from the electrolyte solution, the ion exchanger being only partly saturated with B^+. In this column the electrolyte solution and the exchanger flow in countercurrent to each other. The situation in this column is assumed to be stationary. For working out the methods of calculation we suppose

Fig. 4.

the exchange to be limited to a number of discrete plates at some distance from each other. We can now draw up the material balance for the upper part of the column with n plates.

The basic equations for the material balance for the stationary state are :

total material balance :
$$V_0 + S_{n+1} = V_n + S_1$$

material balance of $A^+ + B^+$:
$$w_0 + u_{n+1} = w_n + u_1 \tag{1}$$

material balance of B^+ :
$$w_0 \cdot X_0 + u_{n+1} \cdot Y_{n+1} = w_n \cdot X_n + u_1 \cdot Y_1 \tag{2}$$

material balance of R' :
$$u_{n+1} \cdot H_{n+1} = u_1 \cdot H_1 \tag{3}$$

Equation (2) can be reduced to

$$Y_{n+1} = \frac{w_n}{u_{n+1}} \cdot X_n + \frac{u_1}{u_{n+1}} \cdot Y_1 - \frac{w_0}{u_{n+1}} \cdot X_0 \tag{4}$$

If it is possible to express the coefficients of X and Y in equation (4) in the ordinate of the diagram in Fig. 5, the operation of the column can be represented graphically.
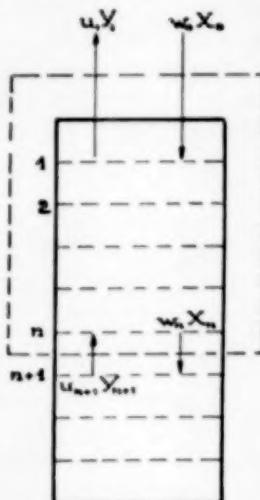
Now :

$u_1 - w_0 =$ the net number of gram eq. of $(A^+ + B^+)$ leaving the top of the column,

$u_1 \cdot H_1 =$ the number of gram eq. of R, leaving the top of the column

$h = \dfrac{u_1 \cdot H_1}{u_1 - w_1} =$ the number of gram eq. of R' leaving the top of the column per gram eq. of $(A^+ + B^+)$.
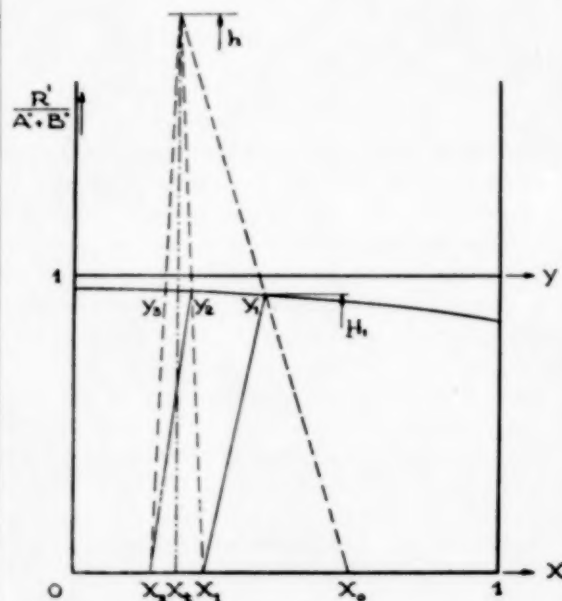

Fig. 5.

The quantity h is expressed in $R'/A^+ + B^+$ and is therefore an ordinate in the diagram referred to.

Now :

$$h = \frac{u_1 \cdot H_1}{u_1 - w_0} = \frac{u_{n+1} \cdot H_{n+1}}{u_{n+1} - w_n} \tag{6}$$

$$(a) \quad \frac{w_n}{u_{n+1}} = \frac{h - H_{n+1}}{h}$$

$$(b) \quad \frac{u_1}{u_{n+1}} = \frac{H_{n+1}}{H_1}$$

$$(c) \quad \frac{w_0}{u_{n+1}} = \frac{H_{n+1} \cdot (h - H_1)}{h \cdot H_1}$$

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Equation (4) then becomes

$$Y_{n+1} = \frac{h - H_{n+1}}{h} \cdot X_n + \frac{H_{n+1}}{H_1} \cdot Y_1 \left. - \frac{H_{n+1} \cdot (h - H_1)}{h \cdot H_1} \cdot X_0 \right\} \quad (7)$$

This equation represents a relation between the co-ordinates of the following points :

$$\begin{aligned} Y_{n+1} &\;; H_{n+1} \\ X_n &\;; 0 \\ Y_1 &\;; H_1 \\ X_0 &\;; 0 \end{aligned}$$

and the ordinate h.

If we draw a straight line through points $(X_0 ; 0)$ and $(Y_1 ; H_1)$ and on this line find the point with ordinate h, we obtain for the abscissa of this point

$$X_t = \frac{h}{H_1} \cdot Y_1 \frac{h - H_1}{H_1} \cdot X_0 = \frac{u_1 \cdot Y_1 - w_0 \cdot X_0}{u_1 - w_0} \quad (8)$$

In equation (7) the terms in X_0 and Y_1 can now be replaced by terms in h and X_t. Equation (7) then becomes

$$Y_{n+1} = \frac{h - H_{n+1}}{h} \cdot X_n + \frac{H_{n+1}}{h} \cdot X_t \quad (9)$$

or :

$$\frac{X_t - Y_{n+1}}{Y_n - X_n} = \frac{h - H_{n+1}}{H_{n+1}} \quad (9a)$$

This equation represents a pencil of straight lines through the points $(Y_{n+1} ; H_{n+1})$ and $(X_n ; 0)$ for any value of n. Point $(X_t ; h)$ is the centre of the pencil. See Fig. 5. The co-ordinates of the pencil point, X_t and h, can at once be calculated from the column quantities by means of equation (6) and (8).

If the plates where exchange takes place are ideal plates, then, by definition, the electrolyte solution running off the plate is in equilibrium with the exchanger moving upwards from it. Graphical construction can now be performed as follows. The top of the column is represented by a line through the points $(X_0 ; 0)$ and $(Y_1 ; H_1)$. This line is a member of the pencil of lines referred to. The ideal plate $n = 1$ is represented by the nodal line through the point $(Y_1 ; H_1)$. The point of intersection of the nodal line and the X-axis indicates the composition X_1. Point $(Y_2 ; H_2)$ is now determined by the point of intersection of the line representing the exchanger and the line through $(X_1 ; 0)$ and the pencil point. See Fig. 5. Thus, by construction, the number of ideal plates can be found which is required to effect the pre-determined separation of the cations. This construction can only be applied as long as the lines through the pencil point do not coincide with the nodal line. If they do, an equilibrium has been established in that portion of the column and no further exchange takes place.

In our continuous percolation column the exchange is not limited to some discrete plates, but takes place continuously for the whole length of the column. The three basic equations (1-3) hold for any cross-section of the column which can therefore be represented by one line from the pencil. By drawing two samples from the electrolyte and two from the exchanger at different levels and analysing these, four points or two lines of the pencil and hence the centre of the pencil can be found. Thus it can be determined what height of the column corresponds with one ideal plate.

In this method of calculation the amounts of gram equivalents of AZ and BZ entrained by the exchanger are fully accounted for. If these quantities are constant throughout the process, then in the diagram the line representing the exchanger is horizontal. The quantity H is then constant and, according to equations (3) and (1), u and w are also constant. From equation (6) follows that $\dfrac{h - H}{h} = \dfrac{w}{u}$; so equation (7) can be written in the form

$$Y_{n+1} = \frac{w}{u} \cdot X_n + Y_1 - \frac{w}{u} \cdot X_0 \quad (10)$$

Now, if quantities v and s are also constant, the equation becomes :

$$Y_{n+1} = \frac{V}{S} \cdot X_n + Y_1 - \frac{V}{S} \cdot X_0 \quad (11)$$

Equation (10) can also be written in the differential form

$$udY = wdX \text{ or } SdY = VdX \quad (12)$$

In the equations only X and Y are variables.

It is therefore possible in a diagram with co-ordinates X and Y to represent the operation of the column. It is also possible to represent the equilibrium condition by an equilibrium line. See Fig. 6. This diagram is analogous to the
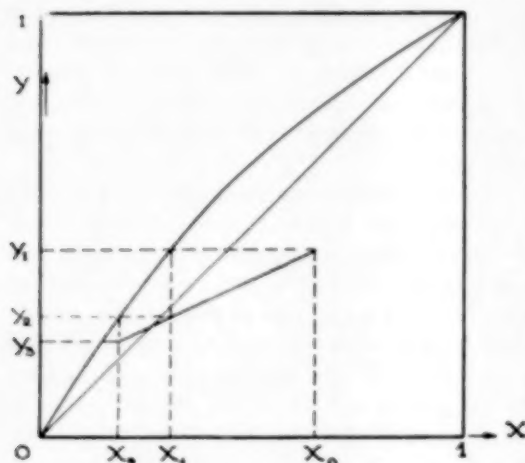

Fig. 6.

vapour-liquid diagram that is used in the calculation of distillation columns according to McCABE and THIELE.

If we now consider Y_{n+1} and X_n as running co-ordinates, then equation (10) represents a straight line in the X-Y diagram. The directional coefficient of this line is given by $\frac{w}{u}$ and one point of the line is given by the co-ordinates Y_1 and X_0. This line is called the operating line. According to the definition of the ideal plate, X_n ; Y_n are in equilibrium with each other. The point $(X_n ; Y_n)$ therefore lies on the equilibrium line. The number of steps that can be constructed between the operating line and the equilibrium line indicates the number of ideal plates represented by the column.

In the continuous percolation column the exchange is again not restricted to discrete plates, but takes place over the whole length of the column. Any cross-section of the column can be represented by a point on the operating line. This appears at once from equation (12).

Thus the simplest graphical method for the calculation of a continuous column operating according to the countercurrent principle has been obtained.

NOTATION

AZ, BZ	= two salts, with cations A^+ and B^+ having the same anion Z'
$(AR + BR)$	= cation exchanger with active groups R' and cations A^+ and B^+
E	= top product
F	= feed
G	= bottom product
$H = \dfrac{R'}{A^+ + B^+}$	= gram equivalent R' per gram equivalent $(A^+ + B^+)$ in the exchanger
$h = \dfrac{R'}{A^+ + B^+}$	= defined by equation (6)
n	= plate number of column
Q	= heat
S	= quantity of exchanger in l./hr.
s	= quantity of exchanger in l. per gram equivalent $(A^+ + B^+)$ in the exchanger
$u = S/s$	= quantity of exchanger in gram equivalents $(A^+ + B^+)$ per hour
V	= quantity of electrolyte solution in l./hr.
v	= quantity of electrolyte solution in l. per gram equivalent $(A^+ + B^+)$ in the electrolyte solution.
$w = V/v$	= quantity of electrolyte solution in gram equivalents $(A^+ + B^+)$ per hour
$X = \dfrac{B^+}{A^+ + B^+}$	= equivalent fraction of B^+ in the electrolyte solution
X_i	= defined by equation (8)
$Y = \dfrac{B^+}{A^+ + B^+}$	= equivalent fraction of B^+ in the exchanger

Indices :

0 and 1	= upper end of column
n and $n + 1$	= lower end of column

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A rapid method of approach to complex distillation problems

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Summary—The method combines slide-rule procedure with graphical plots. Where deviations from ideality have to be taken into account, the approximate magnitude of their effect can be ascertained relatively quickly. In the event that precise plate-to-plate computations are proceeded with, these can be commenced under conditions which are already approximately correct; thereby shortening these often very lengthy and involved computations.

Résumé—Emploi combiné des diagrammes et de la règle à calcul. Lorsqu'on veut en tenir compte, on peut obtenir avec une rapidité satisfaisante les écarts à l'idéalité. Les calculs précis de plateau en plateau peuvent être entrepris à partir de conditions déjà rendues approximativement correctes. D'où une réduction de la durée et de la complication de ces calculs.

While being graphical, much as the familiar McCabe-Thiele diagram for binary mixtures is graphical, the method involves no " smoothing out " of data. Its advantage is that any number of components can be dealt with, each with fundamental algebraic accuracy if desired. Furthermore assuming that the reflux ratio and component fugacities are constant in the system considered, the combined overall effect of (for instance) a combined rectifying-stripping column handling a partially vaporised feed, can be ascertained with precise mathematical accuracy, and relatively rapidly, no matter how many components are present, or how many plates are used. To the extent that reflux ratio and fugacities do in fact vary as between the top of a column, and the bottom, this can be allowed for in a subsequent re-computation; but on first trial one can establish the degree of separation attained by an assumed design, (alternatively the minimum reflux ratio and number of plates to effect the required separation) and then proceed to correct for departures from the ideal. In this initial approach, one does not need to ascertain everything at the same time, and much of the laborious preliminary trial-and-error work, otherwise necessary as for instance in the method of Thiele and Geddes [1] is eliminated.

The method uses a slide-rule pattern of computation; errors here are merely a matter of workmanship. A design is shown in Fig. 1. The base is a drawing-board say 15″ by 12½″ forming a panel on which graphs of foolscap size may be

pinned or clipped down. Two strips of wood are screwed down, forming a channel in which a
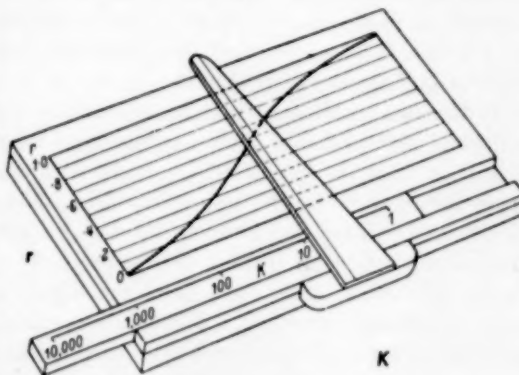

Fig. 1.

strip of wood, carrying a logarithmic scale, can slide. This scale represents K in the familiar equation :

$$y = K \cdot x \qquad (1)$$

where y = molal concentration of a component in the vapour

x = molal concentration of that component in the liquid

K = equilibrium constant characteristic of that component under the conditions of temperature, pressure and mixture composition considered.

The calibration of this log scale, i.e. the number of cycles and extent of close-spacing, may be

chosen to suit the investigation in hand. For the flash vaporisation of crude petroleum for instance, the range of component volatilities is very large, and is often suited by a 5-cycle (1 to 100,000) calibration. On the other hand, for close separation, the entire 15″ length available may be utilised for a single cycle (1 to 10), or even perhaps only a part of that cycle. The scale can readily be made by glueing on to the wood slider, strips of paper cut from commercially available log graph paper ; of course both top and bottom surfaces of each slider can be used ; thus using interchangeable sliders, two or three sliders would provide 4 or 6 calibrations ; only one however (that which gives best use of the plot paper) being in use at one time. A coat of clear varnish saves wear-and-tear of the calibration.

Just as the habit of reading is usually from left to right, so it appears that the habit with distillation problems is to list and deal first with the lightest boiling components. This in fact implies that one uses the K scale with high figures at the left-hand side and low figures at the right-hand side ; so that in the resulting graph, distillate quantities appear in the upper left zone of the graph, and residue quantities in the lower right. The important thing is that the curve used, or to be developed, is drawn against the log scale used. To complete the job, a T-square is required, preferably with a transparent arm with a hairline, similar to an ordinary slide-rule cursor.

Turning now to the mathematical procedure employed ; every worker with algebra is aware that there are often more ways than one of saying the same thing ; by some ways of approach the answer tumbles out simply and compactly ; while by other ways the expression evolved may be cumbersome, though equally valid. Nowhere is this more true than with distillation problems, where the conventional use of x and y as concentration terms of a component in the liquid and in the vapour, respectively, can result in elaborate expressions where the combined Roman and Greek alphabets, capitals and small letters liberally tagged, prove inadequate. In the present case we adhere to what is, in effect, the basic definition of the equilibrium constant or fugacity of a component, K, such that

$$K = \frac{\text{equilibrium molal concentration of a component in the vapour}}{\text{equilibrium molal concentration of that component in the liquid}}$$

Then we follow a pattern using the symbol m for mols of a component in the liquid ; and M for total mols of that component in the system ; so that the amount in the vapour is, by difference, $M - m$. We then simplify by dividing throughout by M, and express the ratio as the term r, such that, for any system, or part of a system

$$r = \frac{\text{mols of a component remaining in the residue}}{\text{total mols of that component present}}$$

We then plot r against a logarithmic scale of K. For a component characterised by a particular equilibrium constant K_1, the algebraic expression to be deduced later for the distillation system considered, will give the value of r_1 ; for another component K_2, the value of r_2 in the same system at the same time ; and so on for any number of components. Thus a smooth curve results. The fact that the curve is smooth does not imply any averaging or smoothing out of data ; on the contrary the curve is the precise locus of a point whose position changes as the only variable, K, changes.

Now these curves all have a useful feature ; because they are plotted on a log K scale, the curve has the same " shape " disregarding the absolute value of K. It will be noted that r and K are both dimensionless, each being a ratio of two quantities ; the identical curve would result if K were expressed in millimetres of mercury or pounds per square inch. It is this constant shape characteristic which enables the slide-rule technique to be used. Such a graph is, in the true sense of the word, a parameter, which has been defined as [2] " a third proportional to the abscissa and any ordinate." That third proportional is in this case whether we are portraying a simple flash vaporisation ; or a rectifying column with three bubble-trays operated at 2 : 1 reflux ratio ; or just what ; its characteristic is the shape and steepness of the curve, which indicate the sharpness or otherwise of the fractionation of the specified system. It tells us that no matter how

many components we have, each and every one of them is represented on it, at some point.

Where experimental data for fugacity are unavailable the same procedure may be used assuming K to be derived from Raoult's and Henry's laws, as the ratio :—

$$\frac{\text{liquid vapour pressure of pure component}}{\text{total gas pressure of system}}$$

We now proceed to develop and exemplify some specific cases.

EQUILIBRIUM CONTINUOUS FLASH VAPORISATION

Let M = mols of a component fed into vaporiser

m = mols of that component left in residue

K = fugacity of that component

V = total mols vaporised = distillate

L = total mols unvaporised = residue

then re-writing equation (1)

$$\frac{M - m}{V} = K \cdot \frac{m}{L}$$

and using reduced units of quantity

$$r = \frac{m}{M}$$

the equation becomes

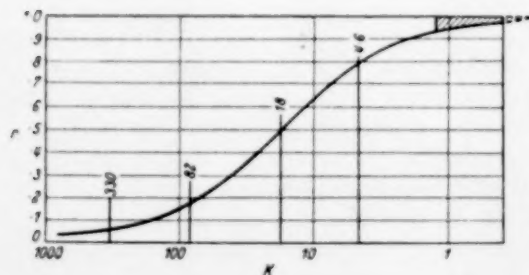$$r = \frac{1}{1 + \frac{VK}{L}} \qquad (2)$$

Fig. 2

This curve is shown in Fig. 2. It does not matter what values one assigns to V or L (other than zero or infinity of course) the curve has the

same shape if V/L were $1/1{,}000$ or $1{,}000$; so for simplicity the points for plotting are :

K	$\dfrac{1}{1 + K} = r$
0·01	0·990
0·05	0·952
0·1	0·909
0·25	0·800
0·5	0·667
1	0·500
2	0·333
3	0·250
5	0·167
9	0·100
19	0·050
99	0·010

The curve is plotted in Fig. 2. It is in fact symmetrical about the point $r = 0.5$.

In the following example, the use of the method to ascertain dew-points of a multi-component mixture is illustrated. The computations involved are no more than are necessary by conventional procedure, but the versatility of the method is developed.

Example 1

A liquid mixture contains :

6 mol % ethane
40 mol % propane
53 mol % butane
1 mol % pentane

It is proposed to pass this through a steam heater to flash off most of the propane and lighter, and separate a residue containing not more than 10% propane. The vaporisation temperature is taken as 60°F. What will the yield be ?

The vapour pressures of the components at 60°F are :—

Ethane	33	atmospheres
Propane	8·2	,,
Butane	1·8	,,
Pentane	0·46	,,

and using a three-cycle logarithmic slider (1 to 1,000) we can conveniently set these off at 4·6, 18, 82 and 330, on the K scale. For initial trial, locating the slider and cursor such that $r = 0.5$

at $K = 18$; (i.e. half the butane remaining) then reading off the other r values :—

	r		M		m
Ethane :	0·05	of original	0·06	=	0·003
Propane :	0·17		0·40	=	0·068
Butane :	0·50		0·53	=	0·265
Pentane :	0·80		0·01	=	0·008
		Total residue		=	0·344

Propane content 0·068/0·344 = 19·7%

Obviously more has to be distilled off, i.e. we must re-locate the slider for lower values of r. However, at these low values the curve becomes asymptotic to the axis $r = 0$ and the values cannot be accurately read on a linear plot. Use may be made of this feature, by plotting r also on a log scale, as in Fig. 3 ; below $r = 0.5$ the r scale is a simple logarithmic one ; and above $r = 0.5$, to avoid a compressed scale when r approaches unity, the curve is a plot of $\log(1 - r)$ so that
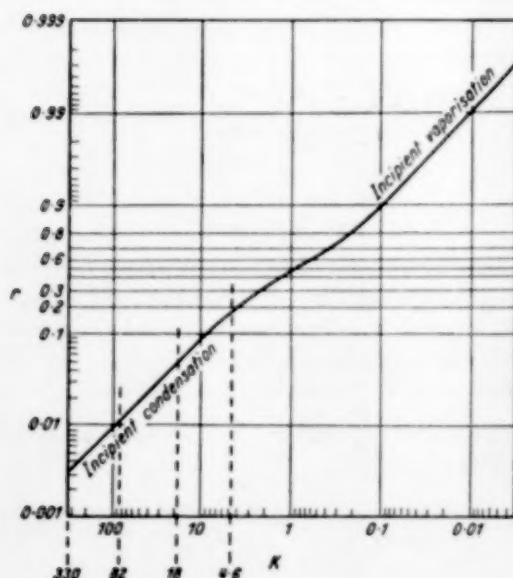

Fig. 3

equal accuracy is obtained at extreme ranges of zero or complete vaporisation. A random trial gives :—

	r		M		m
Ethane	0·003	×	0·06	=	0·0002
Propane	0·011	×	0·40	=	0·0044
Butane	0·05	×	0·53	=	0·0265
Pentane	0·19	×	0·01	=	0·0019
					0·0330

Propane content 0·0044/0·033 = 13·3%

Hence even with only 3·3% residue make, the propane content is too high. Attention may now be drawn to a useful feature of this plot, whereby it is evident that a propane content as low as 10% is in fact unobtainable.

At very low values of r, equation (1) gives a straight-line plot on log-log paper ; this is because K is very high compared with unity, and in the limiting case where the last drop of liquid remains to be vaporised, equation (1) is

$$r = \frac{1}{K}$$

or $rK =$ unity for all components. Thus the limiting case is :

K	$r = 1/K$		M		Proportional amounts in liquid phase
33	0·03	×	0·06	=	0·0018
8·2	0·12	×	0·40	=	0·0480
1·8	0·56	×	0·53	=	0·2960
0·46	2·2	×	0·01	=	0·0220
					0·3678

Minimum propane content : 0·048/0·3678 = 13·1%

The curve is of course valid for equilibrium condensation ; supposing the original mixture had been wholly vapour, and passed through a water-condenser to partially liquefy the least volatiles, the same reasoning applies ; in short the lower left-hand portion of Fig. 3 covers precisely the dew-point region of any mixture.

Incidentally the upper right-hand portion does the same, for vapour in equilibrium with the liquid, just when vaporisation commences. The amount of any component in the vapour is $(1 - r)$ and as $r = \dfrac{1}{1 + K}$.

Amount in vapour $= 1 - r$

$$= \frac{K}{1 + K}$$

When r approximates to unity, K has a very low value; $1 + K$ also approaches unity; hence for all components at the incipient vaporisation point,

$$(1 - r) = K$$

and for purposes of illustration :

K		M		Proportional amounts in vapour
33	×	0·06	=	1·980
8·2	×	0·40	=	3·280
1·8	×	0·53	=	0·956
0·46	×	0·01	=	0·005
				6·221

Maximum propane content in vapour $= 3\cdot280/6\cdot221 = 52\cdot5\%$

Example 2

A crude oil is passed through a pipestill into a flash chamber, where 35 volume per cent distillate is removed. Given the fractional distillation assay of the crude oil, as below, what will be the fractional distillation assay of the distillate ?

Properties of crude oil :

Distilling to	50°F	. .	3·5 vol. % at 760 mm
,, ,,	100°F	. .	5·5 ,, ,, ,, ,,
,, ,,	200°F	. .	11·5 ,, ,, ,, ,,
,, ,,	300°F	. .	20·5 ,, ,, ,, ,,
,, ,,	400°F	. .	29·0 ,, ,, ,, ,,
,, ,,	500°F	. .	37·5 ,, ,, ,, ,,
,, ,,	600°F	. .	46·0 ,, ,, ,, ,,
,, ,,	700°F	. .	54·5 ,, ,, ,, ,,
,, ,,	800°F	. .	63 ,, ,, ,, ,,
,, ,,	900°F	. .	70 ,, ,, ,, ,,
,, ,,	1,000°F	. .	76 ,, ,, ,, ,,

Residue (asphalt) 24 vol. %

The question does not state at what temperature or pressure the vaporisation occurs; assume the temperature to be 400°F to 600°F dependent upon the pressure.

Except for the material boiling below 50°F, which can be considered as butanes, the mixture is a continuous series of hydrocarbons, and in act can be treated as such, using area units forf quantity-volatility units. However, for the initial survey the mixture is considered as composed of twelve components boiling half-way between the temperatures shown, as below ; to each of which is assigned a vapour pressure from generally published data.

Component B. PT. °F	Amount Vol. % = M	Vapour pressure atmospheres	
		= K at 400°F	= K at 600°F
(C₄)	3·5	75	200
75	2·0	50	130
150	6·0	20	80
250	9·0	6·8	35
350	8·5	2·0	15
450	8·5	0·5	5·4
550	8·5	0·11	1·8
650	8·5	0·02	0·6
750	8·5	0·003	0·16
850	7·0	0·0006	0·05
950	6·9	(negligible)	(negligible)
Residue	24·0	(negligible)	(negligible)

We can now commence a preliminary trial, using the graph in Fig. 2 on the slide-rule board in Fig. 1. As reference-point, in locating and fixing the log scale, the 400°F-500°F component group appears suitable by inspection, since it covers the " cut-point " associated with a 35% distillate, and r for this component will fall somewhere in the middle of the r scale where the scale is fairly open for accurate reading.

For this component (mid-point 450°F, $K = 0\cdot5$ at 400°F) we set the K scale such that when $K = 0\cdot5$, r is arbitrarily fixed at 0·4 for preliminary trial.

We then proceed to read off what the value of r is for the other components at their appropriate K values at 400°F, and hence compute distillate composition and quantity as below :

M	r	$1 - r$	Distillate quantity and composition $m = M(1 - r)$
3·5	·006	·994	3·48
2·0	·01	·99	1·98
6·0	·02	·98	5·88
9·0	·05	·95	8·55
8·5	·13	·87	7·40
8·5	·40	·60	5·10
8·5	·75	·25	2·13
8·5	·94	·06	0·51
Heavier (see note below)			0·11
Total			35·14

It will be noted that this setting of K against r results by chance in what is a reasonably acceptable solution, for 35·0% distillate, at first trial. Had the reference point for the 400°F-500°F component been taken as $r = 0.5$, the distillate volume would be too small ; at $r = 0.3$, too large ; and appropriate re-trials would have been required.

It is not necessary to know molecular weights, etc. to ascertain this preliminary product distribution, since $r = m/M$ is dimensionless and has the same value whether m or M are expressed in volume units, weight units, or moles.

In regard to the heavy end " tail " in the distillate shown as 0·11 in the table, this has been assessed as below. Referring to Fig. 2, the shaded area represents those components constituting this " tail," decreasing in amount with increasing boiling point. This area can be estimated by integration from equation (2) and is, very simply,

$$\int_{r=r}^{r=1} (1 - r) \, d \, (\log K) = \log 1/r \qquad (3)$$

The " tail " in the present case covers everything boiling above 700°F. At this point K is by interpolation about 0·008 atmospheres, r is about 0·975, and the integral from $r = 0.975$ to $r = 1.0$ (i.e. from 700°F to zero K) is

$$\log_{10} 1/r = \log_{10} 1.025 = 0.011$$

This is expressed in units of area, a unit area being the product of unit height (r measured from $r = 0$ to $r = 1$) and unit breadth (the distance between any two points K_1 K_2 on the log K scale such that $\log_{10} K_1/K_2 = $ unity, i.e. the length of a 1 to 10 cycle on the K scale).

The " tail " thus represents a quantity of components, which is 0·011 of the quantity represented by such a unit area, at that zone of mixture composition.

The distillation curve of the mixture is relatively flat with say 7 cc spanning every 100°F difference in boiling point. Also this 100°F change represents approximately a five-fold change of K, in this region, as will be seen from the vapour pressure

data. Thus 7 cc or 100°F, occupy $\log_{10} 5 = 0.7$ of a unit length along the K scale. Consequently to cover a unit length along the K scale, the temperature range to be considered should be 100°F/0·7 = 143°F and the unit area represents $7 \times 1.43 = 10$ cc of component quantity. Hence the amount of " tail " is :

$$0.011 \times 10 = 0.11 \text{ cc}$$

If the flash temperature were 600°F instead of 400°F, and if the component volatilities were all raised to the higher level, in equal proportion, such that

$$K \text{ at } 600°F = f K \text{ at } 400°F \qquad (4)$$

the above computation would be precisely as valid for 600°F as for 400°F, if f were constant. However, this is not so. The C_4 vapour pressure has increased threefold but the least volatile components are relatively some 50 or 100 times more volatile than they were. Using the 600°F values for K, the separation at 600°F is poorer than at 400°F, the comparative assay results required being as below :

Flash Vapour Temp.			400°F	600°F
% distilling at		50°F	9·9	9·9
,,	,,	,, 100	15·5	15·5
,,	,,	,, 200	32·3	32·0
,,	,,	,, 300	56·6	55·2
,,	,,	,, 400	77·7	74·6
,,	,,	,, 500	92·2	88·5
,,	,,	,, 600	98·2	95·9
,,	,,	,, 700	99·7	99·0
,,	,,	,, 800	(100·0)	99·8
,,	,,	,, 900	—	(100·0)

The appropriate adjustment, for the specific volatility characteristics, can readily be made. If the distillation were at higher pressure and temperatures, then experimental values of K (expressed in terms of fugacity, rather than vapour pressure) should be used, where available.

CONTINUOUS RECTIFICATION
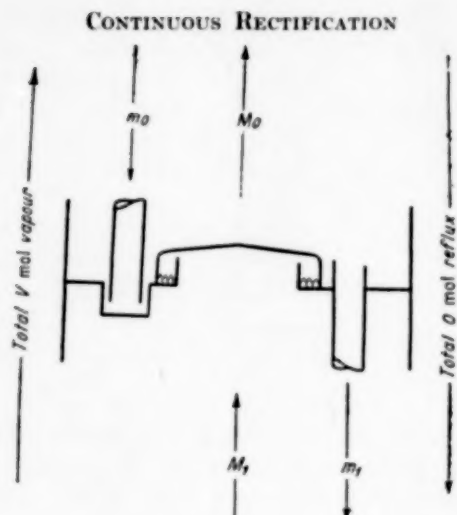
Fig. 4

Component flow rates, mols per unit time, with their derived ratios, are :—

Entering plate as vapour M_1 |
Leaving plate as reflux m_1 | let $\dfrac{m_1}{M_1} = r_1$

Entering plate as reflux m_0 |
Leaving plate as vapour M_c | let $\dfrac{m_0}{M_0} = r_0$

Then the material balance is

$$M_1 - m_1 = M_0 - m_0$$

or rearranging

$$M_o (1 - r_o) = m_1 \left(\frac{1}{r_1} - 1 \right) \qquad (5)$$

Also if the total flow of all components is V mols/unit time upwards as vapour and O mols/unit time downwards as liquid, then using the generally agreed concept of a perfect plate [3], the equilibrium balance for any component (see equation (1)) is

$$\frac{M_o}{V} = K \cdot \frac{m_1}{O} \qquad (6)$$

Dividing (5) by (6) and rearranging gives

$$\frac{1}{1 - r_1} = 1 + \frac{O}{KV} \cdot \frac{1}{1 - r_o} \qquad (7)$$

Similarly for a series of n plates in succession as in Fig. 5

$$\frac{1}{1 - r_1} = 1 + \frac{O}{KV} \cdot \frac{1}{1 - r_o} \quad \text{at 1st plate}$$

$$\frac{1}{1 - r_2} = 1 + \frac{O}{KV} \cdot \frac{1}{1 - r_1} \quad \text{at 2nd ,,}$$

$$\frac{1}{1 - r_3} = 1 + \frac{O}{KV} \cdot \frac{1}{1 - r_2} \quad \text{at 3rd ,,}$$

$$\frac{1}{1 - r_n} = 1 + \frac{O}{KV} \cdot \frac{1}{1 - r_{n-1}} \quad \text{at } n\text{th ,,}$$

Thus by progressive substitution, r_1, r_2, to r_{n-1} can be eliminated ; and r_n can be expressed in terms of r_o and $\dfrac{O}{KV}$. If at the same time $\dfrac{O}{KV}$ can be regarded as constant or given an average value, the summation of a geometrical progression is possible, giving

$$\frac{1}{1 - r_n} \frac{1 - \left(\dfrac{O}{KV} \right)^n}{1 - \dfrac{O}{KV}} + \left(\frac{O}{KV} \right)^n \cdot \frac{1}{1 - r_o} \qquad (8)$$
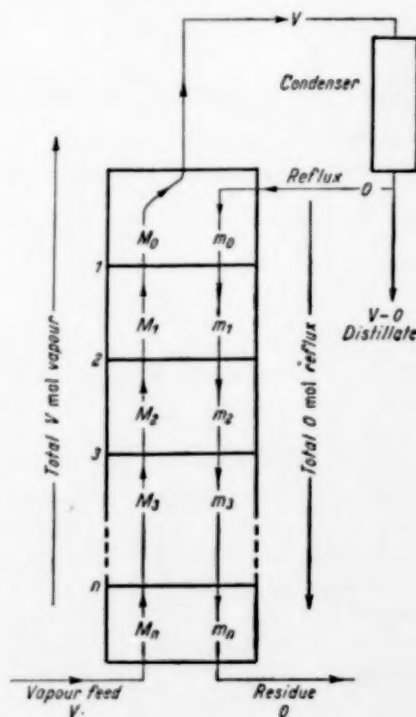

Fig. 5

In Fig. 5, reflux is returned to the head of the column. Of V mols vapour ascending, O mols are returned as reflux liquid to the head. Assuming this liquid to be of the same composition as the ascending vapour,

$$\frac{V}{O} = \frac{m_o}{M_o} = r_o$$

hence

$$\frac{1}{1-r_n} \frac{1 - \left(\frac{O}{KV}\right)^n}{1 - \frac{O}{KV}} + \left(\frac{O}{KV}\right)^n \cdot \frac{1}{1 - \frac{O}{V}} \quad (9)$$

Utilising the concept of reflux ratio,
$R =$ mols reflux returned per mol distillate withdrawn

$$= \frac{O}{V - O} \text{, and}$$

equation (9) may be rewritten

$$\frac{1}{1-r_n} = \frac{1 - \left(\frac{R}{R+1} \cdot \frac{1}{K}\right)^n}{1 - \frac{R}{R+1} \cdot \frac{1}{K}} + \left(\frac{R}{R+1} \cdot \frac{1}{K}\right)^n (R+1) \quad (10)$$

In an ideal system, $\frac{O}{V}$ (or R) and n have the same value for all components, the only variables being r_n and K. For a unit process, the numerical value of $\frac{O}{V}$ or of $\frac{R}{R+1}$, as a coefficient of $\frac{1}{K}$, may be ignored.
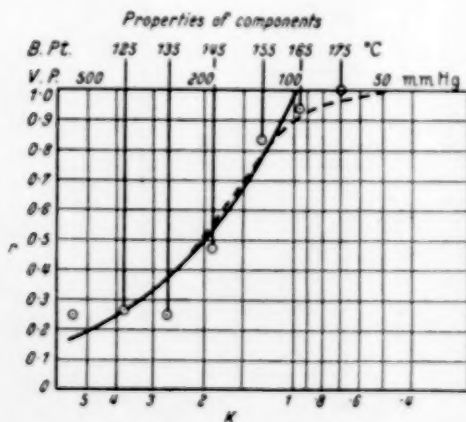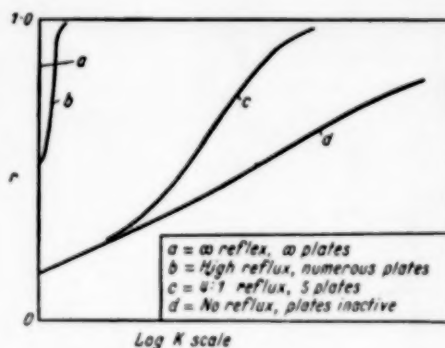
Fig. 6b

Typical curves of equation (9) or (10) are shown in Fig. 6, and their significance is discussed in connection with the first example at the end of this part of the paper. In applying such a curve to find the composition of distillate and residue, only one solution is possible; it is that which gives O mols of residue and $V - O$ mols of distillate. It is not, however, essential to know the molecular weights of the individual components.
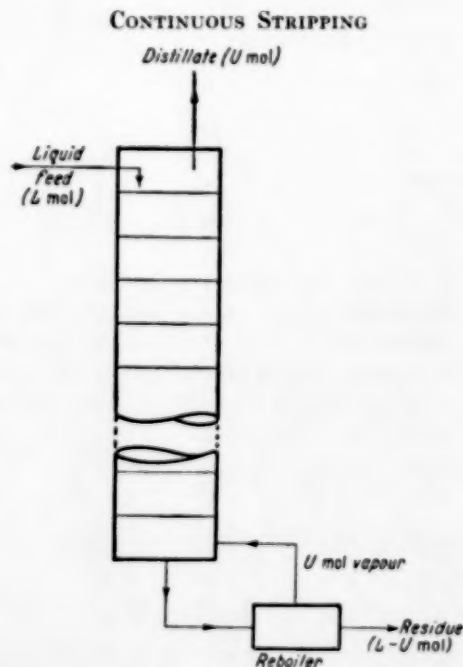
CONTINUOUS STRIPPING

Fig. 6a

Fig. 7

For this unit process, represented in Fig. 7, relationships may be similarly deduced :—

$$\frac{1}{r_s} = \frac{1 - \left(\frac{UK}{L}\right)^n}{1 - \frac{UK}{L}} + \left(\frac{UK}{L}\right)^n \left(\frac{UK}{L-U} + 1\right) \qquad (11)$$

or

$$\frac{1}{r} = \frac{1 - \left(\frac{QK}{Q+1}\right)^n}{1 - \frac{QK}{Q+1}} + \left(\frac{QK}{Q+1}\right)^n (QK + 1) \qquad (12)$$

where U = mols vapour ascending column in unit time

L = mols liquid descending column in unit time

$L - U$ = mols residue withdrawn from base of column in unit time.

Q = revaporisation ratio = $\dfrac{U}{L - U}$

n = theoretical number of plates

and

$$r_s = \frac{\text{mols of that component withdrawn in residue}}{\text{mols of that component fed into column as liquid delivered to the top plate}}$$

The shapes of typical curves for rectification and stripping are shown in Figs. 8a, 8b, respectively. The former trims the "tails" out of

Fig. 8

the overhead, the latter trims the "tops" out of the residue. The overall effect of a combined column such as Fig. 9 combines both properties, and is considered later in this paper. The curve for $r_{overall}$ tends to be as in Fig. 8c.

Example No. 1—GOODLIFFE [4] published some results of tests of a continuous petroleum still. That portion of the still tested constituted a rectifying column, the feed being all in the vapour state, a proportion of fractionated "tops" being withdrawn, and the residue being "white spirit" or "turpentine substitute." The purpose of the column was to secure a residue of satisfactory flashpoint. The system thus constituted a unit process as exemplified by equation (9) or (10). However, the temperature and pressure of the system allowed water to be present in the reflux, and the quantities of hydrocarbons and water constituting the reflux were not measurable and could only be estimated.

The compositions of distillate and residue were ascertained by a distillation assay for true boiling points. In the data shown in Table 1, columns 1, 3, 4 are taken from page 132 of GOODLIFFE's paper, column 2 is taken from Fig. 14 of the same paper, and column 5 is the ratio of column 4 to column 3.

Table 1.

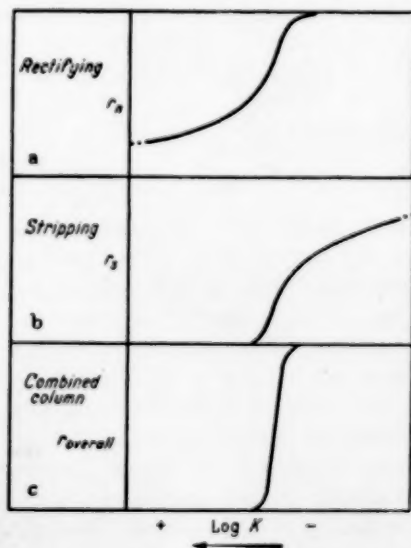| 1	2	3	4	5
Boiling point of component Group, °C	Approximate vapour pressure under conditions in column Mms. Hg.	Mols entering in feed	Mols remaining in residue	$r_{overall}$ Col. 4 = Col 3
Below 120°C	(550?)	0·578	0·146	0·253
120–130	370	1·102	0·292	0·265
130–140	270	2·468	0·613	0·248
140–150	190	3·91	1·9	0·486
150–160	135	9·70	8·14	0·839
160–170	96	9·854	9·25	0·939
170–180	69	5·45	5·45	(1·000)

A curve of column 5, the overall r ratio or "reduced quantity," against the logarithm of column 2, or the "reduced volatility" is shown in Fig. 6a. The column contained 22 plates. Refer-

ring now to equation (9) or (10), provided the term $\dfrac{O}{KV}$ or $\dfrac{R}{R+1} \cdot \dfrac{1}{K}$ is less than unity, then its value to the twenty-second power is negligible; furthermore under such conditions the last term in equation (9) or (10) is also negligible provided $\left(\dfrac{1}{1-\dfrac{O}{V}}\right)$ or $(R+1)$ does not equal infinity, i.e., provided the reflux ratio is not infinite. Under these conditions the equation reduces to $r = \dfrac{O}{KV}$.

Since for a unit distillation process the value of $\dfrac{O}{V}$ makes no difference to the shape of the curve, the curve of this relationship should be "parallel" to that of $r = \dfrac{1}{K}$. The smooth curve drawn through the experimentally observed points is the curve of this equation. It sharply intersects the axis $r = 1.0$, and does not take into account the " tail " of the experimental results, inasmuch as components of boiling point higher than 165°C were found in the tops.

In practice, out of 36·68 mols vapour fed to the column, 29·2 were obtained as residue and 7·48 as distillate, so that the reflux ratio could not have exceeded $29·2/7·48 = 4$. Assuming for the purposes of trial or illustration that the column was equivalent to five theoretical plates, then equation (9) or (10) reduces, as a master curve to

$$\frac{1}{1-r_n} = \frac{1-\left(\dfrac{1}{K}\right)^5}{1-\dfrac{1}{K}} + (4+1)\left(\dfrac{1}{K}\right)^5$$

whence substituting numerical values,

if K is	then r is
10	0·10
5	0·20
3	0·33
2	0·52
1·5	0·70
1·25	0·80
1·111	0·86
1·0	0·90
0·8	0·96
0·5	0·995

These points are plotted as the dotted curve in Fig. 6a.

Comments on the above example

(1) The compositions of distillate and residue are determined as much by the plant, a unit rectifying process, as by the reflux ratio, or by the number of efficiency of the plates. The reflux leaving the bottom tray, constituting the residue leaving the system, cannot be fractionally stripped of light ends, since it has just been brought to equilibrium with the incoming vapours. It must, therefore, be saturated with incoming vapours, approximately in accordance with equation (2).

For high values of K, equation (2) becomes $r = \dfrac{1}{K}$, as deduced also from equation (10) and plotted in Fig. 6a. On the other hand, the distillate is stripped of heavy ends, and it is only here that the fractionating effect of reflux and number of plates becomes apparent.

(2) It might be concluded, therefore, that reflux ratio appears to have little influence on fractionation. This is not the case. For the particular unit distillation process considered, increased reflux can only be obtained by reducing the yield of distillate and increasing the yield of residue. This has the effect, first of displacing the curve for r to the left, making the areas (or verticals) representing these yields change according to yields; and secondly, of increasing the value of $(R+1)$ in equation (10) (or $\dfrac{1}{1-\dfrac{O}{V}}$ in equation (9)). The effect is illustrated in Fig. 6b; at total reflux and with an infinite number of plates, the curve is a vertical straight line. As the yield is increased, the reflux ratio decreases until at zero plate number, where reflux quantity is unimportant since there are no plates upon which to work (i.e., at equilibrium flash condensation, giving the same component distribution as equilibrium flash vaporisation), equation (2) applies directly.

(3) It may be doubted whether the efficiency of the true boiling-point assay used was sufficient for separation of components boiling 10°C apart; the method used is inferior to that of PETERS [5],

or PODBIELNIAL [6]. Only a smooth curve drawn through the experimentally observed points, therefore, is of significance, and unless the " tail " of the curve, i.e., the content of heavy ends in the tops, is accurately determined an accurate estimate of tray efficiency is not possible.

(4) The relative volatility scale in Fig. 6a, may be correlated with component volatilities under conditions in practice. Thus the curve for an infinite number of plates gives $r = 1.0$ for a component with a vapour pressure of 100 mms Hg. The distillation was under a pressure of about 870 mms Hg, so that assuming Raoult's Law, the value of K is $\frac{100}{870} = 0.115$. The total mols vapour ascending the column, steam and hydrocarbons, was 112, while the reflux consisted of 12 mols hydrocarbon. Thus $O/KV = 12/0.115 \times 112 =$ approximately unity in accordance with theory.
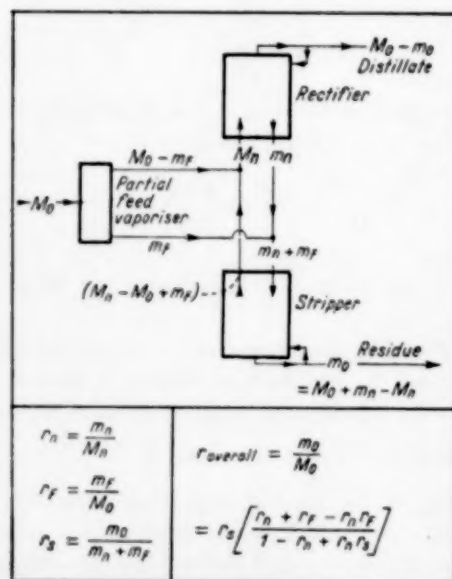
COMBINED DISTILLATION PROCESSES

Fig. 9

In practice the feed to the combined rectifying-stripping column, Fig. 9, may be partially vaporised, and the system could be considered in three sections :—

1. *Flash Vaporisation of Feed*—Knowing the proportion vaporised, r in equation (2) can be calculated for various values of $\frac{VK}{L}$, using for this purpose the values of V, L, and K obtaining. This r can be denoted as r_F.

2. *Rectifying Section*—Similarly using the values of O, V, n, and K, obtaining in equation (9), values of r_n may be ascertained for the same component.

3. *Stripping Section*—Similarly using the values of U, L, n, and K, in this section, values of r_s may be found by equation (11).

On a material flow balance, these three values of r are simultaneous for any one component, since neither gain nor loss of material occurs in the system. From a material balance the overall effect of the entire system may be arrived at :—

$$r_{overall} = \frac{\text{quantity of a component in residue}}{\text{quantity of a component in feed}}$$

$$= r_s \left(\frac{r_n + r_F - r_n r_F}{1 - r_n + r_n r_s} \right) \quad (13)$$

The steps involved in deducing this equation are those of simple algebraic substitution, eliminating the M and m terms (see Fig. 9). The equation reduces to simpler form if the feed is all liquid ($r_F =$ unity) or all vapour ($r_F =$ zero).

Infinite Number of Plates and Critical Reflux Ratio—Where a very large number of plates is used, then for values of $\frac{O}{KV}$ less than unity, $\left(\frac{O}{KV} \right)^n$ becomes negligibly small and equation (9) for a rectifying section reduces to

$$r_n = \frac{O}{KV} \quad (14)$$

The curve, Fig. 10, intersects the straight line $r = 1.0$ when $\frac{O}{KV}$ is unity ; values of r greater than unity are imaginary.

Similarly, the stripping equation (11), when $\frac{UK}{L}$ is less than unity, reduces to

$$r_s = 1 - \frac{UK}{L} \quad (15)$$

the curve of which is also shown in Fig. 10.

The overall r curve is given approximately by a straight line joining the two points AB. More accurately the curve could be found by using equation (13). Assuming for the purposes of
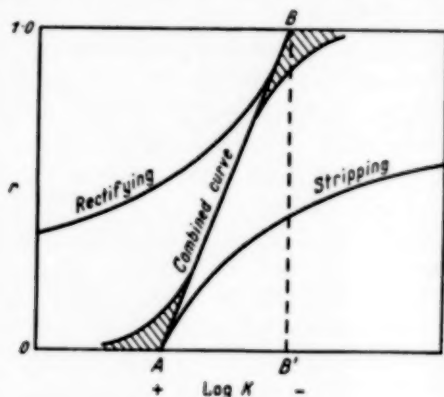

Fig. 10

illustration that the feed is liquid ($r_F =$ unity), then $U = V$ and $L = O + F$; and assuming that the value of K for a component is the same throughout the system, then equation (13) for an infinite-plate column reduces to

$$r_{overall} = \frac{1 - \dfrac{VK}{O + F}}{1 - \dfrac{O}{O + F}}. \qquad (16)$$

As has been stated, the steepness of the r curve is an indication of the sharpness of fractionation obtained. The distance AB' thus affords an index of this sharpness; it may easily be found from equation (16) by substituting $r = 0$ whence $K = (O + F)/V$; and $r = 1$ whence $K = O/V$; therefore $A - B' = \log(O + F)/V - \log O/V = \log \dfrac{O + F}{O}$.

The distance can only be zero, i.e., the r curve can only be a vertical straight line when F is negligibly small in comparison with O; that is, at total reflux. At finite reflux ratios, the separation of components which can be realised, even with an infinite-plate column, is determined by the length AB', which equals $\log \dfrac{O + F}{O}$.

The effect of the number of plates can be clearly

demonstrated. Increasing the number of plates in the stripping section decreases the shaded area in the lower left-hand portion of Fig. 10 ; similarly, the number of plates in the rectifying section affects the shaded area in the upper right-hand portion. The maximum steepness obtainable is determined not by the number of plates, but by the value of $\dfrac{O + F}{O}$. This is of use in problems of design. Assuming that the sharpness of fractionation required has been decided upon, then there is a certain critical value of $\dfrac{O + F}{O}$. below which no increase in column height will fulfil requirements. It is to be expected that the degree of separation obtained by a combined column is dependent not upon the reflux ratio, nor the revaporisation ratio alone, but upon the combined effect of these ratios. By definition

$$\frac{O}{V} = \frac{R}{R + 1}$$

$$\frac{U}{L} + \frac{Q}{Q + 1}$$

and for the simplified case considered in deriving equation (16), substitution gives

$$\frac{O + F}{O} = \frac{(R + 1)(Q + 1)}{RQ} \qquad (17)$$

Thus the ratio $\dfrac{O + F}{O}$ includes the effect of both R and Q, irrespective of the numerical value of either. In problems of design, a known, or assumed, proportion of input material is required as distillate ; and if the value of $\dfrac{O + F}{O}$ corresponding to the desired degree of separation is known, then both R and Q must possess certain values. For instance, if the mol fraction required in the distillate is G

$$G = \frac{V - O}{F}$$

and if a degree of separation corresponding to $\dfrac{O + F}{O} = H$ is required then,

$$R = \frac{O}{V - O} = \frac{1}{G(H - 1)} \qquad (18)$$

$$Q = \frac{V}{O + F - V} = \frac{H}{(1 - G)(H - 1)} \qquad (19)$$

As a further example, Thiele and Geddes give a detailed calculation for a petroleum mixture assessed as containing 19 components, and distilled continuously under the conditions given in Table 2.

Table 2

		Flow rate, Mols/hr, mixed components		
		Liquid	Vapour	Temp. °F
	Distillate	—	610	—
Rectifying	1st plate	212	822	322
	2nd plate	208	818	355
		208	818	
		261 ←———(261)		
	Feed (cold)	806	—	
		1275	1079	
Stripping	One plate	1275	1079	365
	Reboiler	1275	1079	435
	Bottoms	196	—	

The method used by Thiele and Geddes gives the results in Table 3, columns 1, 2, 3, and 5 of which are taken from their paper.

The figures in column 4 of Table 3 have been calculated from the data given, being from the ratio

$$\frac{\text{mols of a component in the residue}}{\text{mols of that component in the feed}}$$

while column 6 gives the approximate mean value of $\log_{10} K$ in the system, the average temperature

of which is about 365°F. Since Raoult's and Dalton's Laws are assumed and the distillation is under a total pressure of 760 mm Hg, K in equation (1) is equal to the vapour pressure divided by 760 mm.

Table 3

1	2	3	4	5	6
	Rates of flow mols/hr			Volatility of Component	
Boiling point of Component	In feed	In residue	Ratio r ($\frac{Col. 3}{Col. 2}$)	V.P. at 365° F mms Hg	$\log_{10} \frac{V.P}{760}$
− 135	2·67	0·000009	—	—	—
− 49	21·80	0·0004	—	—	—
12	19·13	0·0012	—	—	—
32	47·75	0·004	—	—	—
97	56·90	0·013	—	—	—
153	70·34	0·054	< 0·001	11,100	1·164
207	86·00	0·22	0·003	5,800	0·882
254	83·90	0·68	0·008	3,220	0·627
298	68·55	1·69	0·025	1,825	0·380
340	62·50	4·44	0·071	1,060	0·144
369	44·22	7·07	0·160	710	− 0·030
393	41·08	12·48	0·300	507	− 0·176
415	45·45	22·40	0·493	369	− 0·314
435	37·36	26·07	0·697	275	− 0·442
453	35·72	29·90	0·840	212	− 0·555
472	31·42	29·25	0·929	156	− 0·688
492	24·88	24·19	0·972	119	− 0·805
517	21·13	21·00	0·994	77	− 0·995
547	4·39	4·387	> 0·999	46	− 1·218

A graph of r against $\log K$, from the data in Table 3, is given in Fig. 11. The curve in Fig. 11 may be arrived at by the methods outlined previously. The average temperature of the stripping section is, say, 400°F, and of the rectifying section 340°F. Reference to data for the vapour pressure of hydrocarbons shows that a component having a volatility of K in the stripping section (400°F) will have a volatility of $0.4 K$ in the rectfiying section (340°F); this is correct only for a component with a boiling point of about 400°F, but it is here assumed to be true for all the component.

Applying equations (9) or (10) to average conditions in the rectifying section

$$\frac{O}{V} \cdot \frac{1}{K} = \frac{210}{820} \cdot \frac{1}{0.4\,K} = \frac{0.64}{K}$$

$$n = 2$$

$$R = \frac{210}{610} = 0.35$$

$$(R + 1) = 1.35$$

and $\dfrac{1}{1 - r_n} = 1 + \dfrac{0.64}{K} + \dfrac{0.55}{K^2}$

whence values of r_n for various values of K can be found.

Applying equations (11) or (12) to average conditions in the stripping section

$$\frac{UK}{L} = \frac{1079}{1275} \cdot K = 0.85\,K$$

$$n = 1$$

$$Q = \frac{1079}{196} = 5.5$$

and $\dfrac{1}{r_s} = 1 + 0.85 + 4.7\,K^2$

whence values of r_s for various values of K can be found.

Applying equation (13) for the case of a feed consisting entirely of liquid ($r_F = 1.0$),

$$r_{\text{overall}} = \frac{r_s}{1 - r_n + r_n r_s}$$

whence r_{overall} may be calculated. The results so obtained are given in Table 4.

Table 4

K	r_s	r_n	r_{overall}
0.1	0.917	0.984	0.999
0.3	0.596	0.891	0.93
0.5	0.385	0.777	0.74
0.7	0.257	0.671	0.51
1.0	0.153	0.543	0.28
2.0	0.047	0.315	0.07
4.0	0.013	0.163	0.016
10.0	0.002	0.065	0.002

These results are plotted in Fig. 11. It is however not the close agreement – in fact the identity for most practical purposes – which is of significance. That is a foregone conclusion, since the basic mathematics are the same ; in fact had the more detailed expression
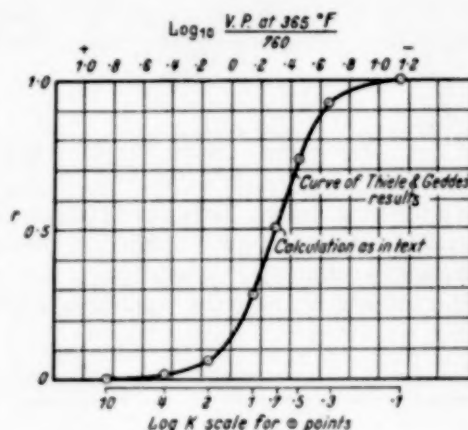

Fig. 11

$$1 + \frac{O_1}{K_1 V_1} + \frac{O_1 O_2}{K_1 K_2 V_1 V_2} +$$

been used instead of the summation term in equation (8), employing average values for O, K, and V, the two results would be mathematically identical. What is significant is the rapidity and directness of the method as compared with the conventional procedure ; any number of plates can be handled with as much facility as two or three, and any number of components dealt with simultaneously.

Apart from its use for predicting performance, taking the " theoretical plate " as yardstick, the method is also of use for assessing plant results. From an analysis of distillate and residue, an experimental r versus log K curve can be plotted, and that value of n, giving the best fit to the results, can be ascertained.

For total reflux the same procedure of plotting r versus log K may be followed. In this case r is taken as the ratio

$$\frac{x}{x + y}$$

where x is the concentration of a component in the liquid in the still base, and y its concentration in the distillate. The relationship is

$$r = \frac{1}{1 + K^{n+1}} \qquad (20)$$

where n is the number of plates. This follows directly from the conventional relationship

$$y = K^{n+1} x$$

for total reflux equilibrium. One may either draw curves to suit a specific case, based on equation (20), or use the curve for flash vaporisation in Figs. 2, 3, with the log scale opened up to suit the number of plates. The equation for flash vaporisation is the same as for equation (20) except that n is zero. Thus where the distance from 1 to 10, for single-stage vapour/liquid equilibrium, was say d inches, it now becomes :

for 2 stages (1 plate)   .. $2d$ inches
,, 3   ,,   (2 plates)   .. $3d$,,
,, 4   ,,   (3 plates)   .. $4d$,,
    etc.

Not infrequently a large temperature gradient exists in such columns, and the relative volatilities of the components are not the same at the top as at the bottom. However, one could calculate r with a progressively changing K as we ascended the column.

The general procedure of plotting r against $\log K$ is also applicable to batch distillation. More than one combination of number of plates and reflux ratio is possible to achieve a desired degree of fractionation ; and the concept of " overlap coefficient," or average area in which heavy ends in the distillate or light ends in the residue are to be found, above and below the point $r = 0.5$, serves as a useful correlation index for the approximate equivalence of alternatives. It is hoped to deal with these subjects in a later paper.

ACKNOWLEDGMENT

NOMENCLATURE

n = number of theoretical plates in section of column considered.

R = reflux ratio
   = mols reflux returned to column head per mol-distillate withdrawn

Q = revaporisation ratio
   = mols vapour ascending from column base per mol-residue withdrawn.

x = molal concentration of a component in liquid, in equilibrium with vapour

y = molal concentration of same component in vapour

$K = \dfrac{y}{x}$ for that component

O = molal flow rate of total liquid descending rectifying column or portion of column

V = molal flow rate of total vapour ascending rectifying column or portion of column.

L = molal flow rate of total liquid descending stripping column or portion of column

U = molal flow rate of total vapour ascending stripping column or portion of column

F = molal flow rate of total fresh feed material entering system

M = molal flow rate of an individual component in vapour or in feed mixture

m = molal flow rate of an individual component in liquid or in residue from completed distillation process.

$r = \dfrac{m}{M}$

$r_n = \dfrac{\text{mols of a component in reflux leaving bottom plate of a rectifying column}}{\text{mols of that component in vapour entering bottom plate of a rectifying column}}$

$r_s = \dfrac{\text{mols of that component in bottoms withdrawn from base of stripping column}}{\text{mols of that component in liquid feed delivered to top plate of a stripping column}}$

$r_F = \dfrac{\text{mols of that component entering system as liquid feed}}{\text{mols of that component entering system as total (liquid plus vapour) feed}}$

$r_o = r_{\text{overall}} = \dfrac{\text{mols of that component in residue from completed distillation process}}{\text{mols of that component entering system as fresh feed}}$

$= $ a function of r_n, r_s, and r_F

As subscripts, 1, 2, 3 . . . . . . n indicate quantities at first, second . . . . . . nth plate

s indicates quantities in stripping section

F indicates quantities in flash vaporisation unit.

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The catalytic destructive hydrogenation of paraffin wax

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Summary—1. When heating paraffin wax in an autoclave in the presence of high pressure hydrogen at 450°C during one hour as described below, approx. 30% by weight of this wax is converted into hydrocarbons boiling below 100°C.

2. Under identical conditions but in the presence of hydrogenation catalysts the conversion into lower hydrocarbons was far more pronounced. For instance, by the use of tungsten disulphide as hydrogenation catalyst even 75% by weight of the wax was converted into hydrocarbons boiling below 100°C.

Moreover the quality of the reaction products was different. In the experiments in the presence of hydrogenation catalysts these products were far more or completely saturated and the formation of cyclic compounds was very low in comparison with the products of hydrogenation without a catalyst.

The catalysts used were : nickel on guhr (i.e. kieselguhr), tungsten disulphide, colloidal molybedunum on active carbon and molybdenum trioxde.

3. By the use of SiO_2-Al_2O_3 cracking catalyst under otherwise identical conditions conversion into lower hydrocarbons was also increased as compared with the experiments mentioned under 1. The products, however, were more unsaturated but they contained about the same amount of rings per molecule, that is approx. 0·3.

4. By the use of mixed type catalyst the conversion as well as the quality of the products were between those of the experiments mentioned under 2 and 3.

Résumé—1. Par chauffage à 450°C de la paraffine solide en présence d'hydrogène sous haute pression, les auteurs en ont transformé 30% environ en hydrocarbures, bouillant au dessous de 100°C.

2. Dans les mêmes conditions, mais en présence de catalyseurs d'hydrogénation, le craquage est beaucoup plus accentué, par example, avec WS_2, 75% de la paraffine sont convertis en produits bouillant au dessous de 100°C. L'emploi de catalyseurs d'hydrogénation modifie à la fois le rendement et la qualité des produits. Ces derniers sont entièrement ou presque totalement saturés, la production de produits cycliques devenant très faible. Catalyseurs essayés : nickel, sulphure de tungstène, molybdène colloïdal sur charbon actif, trioxyde à molybdène.

3. En présence de SiO_2-Al_2O_3 comme catalyseurs, le craquage est plus accentué qu'en essai 1. les produits obtenus sont moins saturés tout en conservant approximativement la même proportion d'anneaux par molécule. (0·3 environ).

4. Un catalyseur mixte donne des résultats intermédiaires entre ceux qui correspondent aux essais 2 et 3.

INTRODUCTION

The destructive hydrogenation of organic substances has first been studied by BERGIUS [1] who intended to transform materials with a low hydrogen content such as coal, tar, etc., into products richer in hydrogen. The process used consisted of heating these materials under high hydrogen pressures (above 100 atm.), at temperatures ranging from 400-500°C, *without the use of catalysts*. BERGIUS called this process " berginization," which process formed the basis of the catalytic coal liquefaction process later on worked out by *I. G. Farben*.

As BERGIUS always used in his experiments a few per cent of iron oxide which he added, according to his explanation, to remove sulphur and not as a catalyst necessary to accelerate the addition of hydrogen, some doubts originally existed about the possibility of adding hydrogen to a molecule without the use of a catalyst.

Two of the authors (WATERMAN and PERQUIN) in collaboration with others [2] have proved that hydrogen could be fixed without the addition of a catalyst to a molecule which under the conditions of the experiments was split into fragments. To study the reaction on

less complicated molecules they chose paraffin wax as a base material and compared it with a heat treatment without the use of hydrogen (cracking).

In continuance of these initial experiments larger quantities of the reaction products were submitted to a more detailed investigation [3] in order to obtain a better insight into their composition. For this purpose use was made of the at that time newly-developed graphical statistical analysis of hydrocarbons by means of the so-called ring analysis [4].

The results of this investigation showed that the products obtained by destructive hydrogenation (berginization) of paraffin wax at 450°C were less cyclic in nature than those obtained by cracking experiments at the same temperature. The use of nickel on guhr in the experiments under high hydrogen pressure, which was a further step in the study of these processes, produced products completely free from cyclic hydrocarbons.

In this paper some further experiments on the destructive hydrogenation of paraffin wax are described, in which the influence of different catalysts was investigated, especially with respect to the properties of the liquid reaction products. The catalysts used were well-known hydrogenation catalysts such as Ni on guhr, MoS_2, MoO_3 and WS_2 and also a synthetic cracking catalyst Al_2O_3-SiO_2 prepared by hydrolysis of a mixture of aluminium isobutylate and silicium tetraethylate. Also a mixed type catalyst was used prepared by coprecipitation of MoS_2, Al_2O_3 and SiO_2. Pure white Rangoon paraffin wax of mol. weight of 360 was again chosen as the base material.

EXPERIMENTAL PART

a. Preparation of Catalysts.

SiO_2-Al_2O_3 : 8·4 grams of aluminium isobutylate were dissolved in 121·6 grams of silicium tetraethylate by gentle heating. 140 ml of distilled water were added in approx. 10 minutes and the mixture was stirred intensively during 20 minutes, the temperature being kept at 60°C. After flocculation the mass was dried at 100°C for 2 hours and thereafter in an electric furnace at 400°C for 4 hours.

Nickel on guhr : 500 grams of Ni $(SO_4)_2$·7 aq. were dissolved in 1·5 litres of distilled water and 500 grams of guhr added. The suspension was heated to the boil and a solution of 200 grams of Na_2CO_3 in 750 ml of water (100°C) added under stirring. After boiling for some time the mass was filtered and washed repeatedly by boiling with distilled water and filtration, until negative SO_4'' reaction in the wash-water. The catalyst was dried at 120°C and reduced at 550°C in a hydrogen stream.

Molybdenum on charcoal (5): To 15 grams of ammonium molybdate dissolved in 400 ml of water were added 100 ml 3·4 N sulphuric acid. The solution was heated nearly to the boil and H_2S was introduced to reduce the molybdenum, forming a blue colloidal sol. The solution was completely decolorized by adsorption of the colloidal material on 40 grams of active carbon. The catalyst was filtered off, washed with small amounts of water and dried at 90-100°C.

Mixed type catalyst : This catalyst was prepared by hydrolysing a mixture of 30·4 grams of silicium tetraethylate and 2·1 grams of aluminium isobutylate with a colloidal MoS_2 solution (prepared by reducing 3·2 grams of ammonium molybdate with H_2S in dilute sulphuric acid as described above) at approx. 60°C, filtration, drying at 100°C and heating in an electric furnace during 4 hours at 400°C.

A WS_2 catalyst was obtained from the *Koninklijke/Shell-Laboratories* at Amsterdam; pure MoO_3 from the Inorganic Chemistry Laboratory of the Technological University at Delft.

b. Destructive Hydrogenation.

The experiments were carried out in rotating autoclaves of $\frac{1}{2}$ litre and 2 litres volume. After filling the autoclaves with the weighed amounts of paraffin wax and catalyst hydrogen was introduced to an initial pressure of approx. 100 atm.

It is essential to heat up the autoclaves to the reaction temperature in as short a time as possible. In our experiments the temperature was raised to 240-260°C in about 15 minutes, and after that, by using two series of gas burners, to the reaction temperature (450°C) in 15-18

TABLE

Destructive hydrogenation of Rangoon paraffin wax, average mol. weight 360.

Expt. No.	base materials			reaction conditions			reaction products wt % on base materials				bromine number of liquids		Selected analysis of distillation fractions of saturated liquid reaction products ****			
	paraffin wax grams	Hydrogen initial pressure (atm.)	catalyst grams	reaction time min.	temp. °C	max. pressure atm.	boiling point <100°C	boiling point 100-200°C	boiling point >200°C	un-accounted for	before saturation	after saturation	n_D^{70}	d_4^{70}	r_D^{70}	mol. weight
1	300	120	no catalyst	60	450	—	31	19	40	10	approx. 12	—	1·3940 1·4104 1·4251 1·4302 1·4334	0·6975 0·7301 0·7557 0·7677 0·7740	0·3430 0·3396 0·3571 0·3360 0·3361	94 101 144 162 175
2	300	100	15 g SiO$_2$-Al$_2$O$_3$	60	450	280	46	26	22	4	34	0·2	1·4005 1·4060 1·4141 1·4169 1·4276 1·4358 1·4423	0·7092 0·7228 0·7398 0·7453 0·7653 0·7811 0·7913	0·3422 0·3398 0·3378 0·3373 0·3359 0·3341 0·3346	95 107 156 187 246
3	75	100	8 g Ni-guhr	60	450	250	53	31	33	3	0·0	•••	1·3922 1·4060 1·4214 1·4282 1·4321	0·6695 0·7231 0·7477 0·7627 0·7689	0·3455 0·3416 0·3375 0·3375 0·3374	104 129 150 188 213
4	300	78	20 g WS$_2$	30	450	210	57	27	12	4	1·9	0·3	1·4078 1·4151 1·4219 1·4270 1·4325 1·4407 1·4288**	0·7251 0·7396 0·7532 0·7622 0·7727 0·7866 0·7698**	0·3401 0·3387 0·3373 0·3369 0·3360 0·3347 0·3396**	— 155 198 249 309
5	300	90	30 g WS$_2$	60	450	250	74	18	3	5	0·8	•••	1·3970 1·4029 1·4060 1·4206	0·7035 0·7157 0·7308 0·7527	0·3423 0·3409 0·3363 0·3366	100 117 185
6	75	100	10 g MoS$_2$ on carbon	60	450	240	30	29	37	4	0·0	•••	1·4013 1·4149 1·4174 1·4246 1·4370	0·7094 0·7387 0·7415 0·7542 0·7625 0·7797	0·3427 0·3406 0·3394 0·3383 0·3378 0·3360	114 168 184 198 239
7	150	100	8 g pure MoS$_2$	60	450	250	57	27	12	4	2·6	0·1	1·3858 1·4005 1·4060 1·4194 1·4278 1·4641	0·6799 0·7079 0·7207 0·7459 0·7614 0·7785	0·3453 0·3428 0·3408 0·3388 0·3374 0·3367	99 108 163 185 226
8	300	98	17 g mixed SiO$_2$-Al$_2$O$_3$, Mo	60	450	280	49	35	13	3	12	0·1	1·3925 1·3994 1·4087 1·4107 1·4257 1·4291 1·4409	0·6952 0·7093 0·7277 0·7499 0·7614 0·7661 0·7880	0·3429 0·3413 0·3395 0·3373 0·3363 0·3366 0·3346	94 130 165 188 235

* 70°C, calc. for 20°C.
** not saturated.

**** The total number of fractions was large; the selected fractions are however representative for the whole distillate.
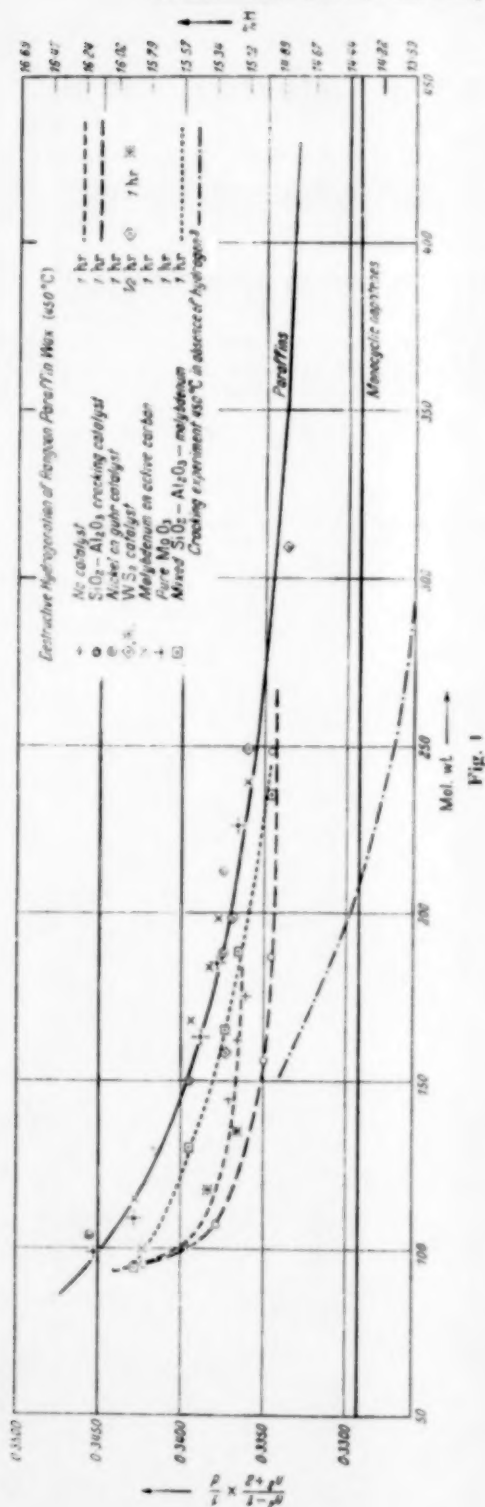
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Fig. 1

minutes. The proper reaction time was 1 hour in most cases, during which the temperature, measured by means of a gauged thermocouple reaching into the centre of the autoclave, could be kept constant within 3°C. After reaction cooling was performed by means of air blowing until room temperature was reached.

The gaseous reaction products together with the greater part of low boiling hydrocarbons with 5 and 6 carbon atoms were removed from the autoclave by blowing the gases off. After normal pressure had been reached the autoclave was evacuated to about 60 mm mercury pressure by the use of a Töpler pump.

After opening of the autoclave the contents were poured out and the autoclave rinsed with pentane. The catalyst was extracted with pentane in a Soxhlet apparatus and finally the solvent was distilled off from the combined solutions in a fractionating column.

As the main purpose of these experiments was to investigate the properties of the liquid products no effort has been made to collect all the reaction products quantitatively.

Unsaturation of the liquid reaction products was roughly estimated by means of the bromine value (MCILHINEY); when this value exceeded 1, the products were saturated by a careful hydrogenation (approx. 280°C, 200 atm. of hydrogen, 20% of a nickel on guhr catalyst). The saturated products were fractionated into a number of fractions, of which several physical constants were determined as collected in Table I.

Structural analysis of the fractions by means of the ring analysis is shown in Fig. 1. In this figure their ring content can be easily estimated by interpolation between the curves for the paraffins (no rings) and for the monocyclic naphthenes (1 ring per molecule).

DISCUSSION OF RESULTS

A drawback in the batch process described with the use of autoclaves for these experiments is that the amount of hydrogen to be added to the reaction is limited by the maximum allowable pressure in these autoclaves. Therefore the initial pressure could not exceed 120 ats. Another handicap is that the experiments cannot be

carried out at a constant hydrogen partial pressure. It is therefore possible that in cases where a large hydrogen consumption takes place the partial pressure will be too low at the end of the reaction period to fully saturate the molecular fragments so that they have the opportunity to polymerize or cyclicize.

The results obtained are therefore not final although they give a reasonable idea of what happens during these reactions. It is therefore the intention to finalize them by using a continuous procedure.

The following conclusions can be drawn :
1. Destructive hydrogenation of paraffin wax at 450°C in the *absence of catalysts* leads, in accordance with former experiments [3], to hydrocarbons of lower molecular weight, being relatively unsaturated and only partly cyclic in nature (average ring content approx. 0·2-0·3 rings per molecule). However, only approx. 50% of the starting material is transformed into products boiling below 200°C in a 1 hour experiment.
2. Application of an SiO_2-Al_2O_3 cracking catalyst increases the formation of products of lower molecular weight, the cyclic nature of the reaction products, however, not being far more pronounced.
3. Several hydrogenation catalysts (nickel on guhr, MoS_2 on active carbon) lead to fully saturated reaction products, which are not cyclic.
4. In the case of WS_2 the strongly pronounced cracking activity should be mentioned : the starting material is nearly completely transformed into products boiling below 200°C in 1 hour. This catalyst at the same time favours hydrogenation, the reaction products being almost fully saturated. Cyclization occurs to some extent in the lower molecular reaction products only, perhaps due to lack of hydrogen in the latter stage of the reaction.
5. Application of pure MoO_3 gives rise to non-cyclic cracking products, these being unsaturated to a small extent.
6. The use of a mixed type SiO_2-Al_2O_3-molybdenum catalyst leads to products, which according to their cyclic nature, are in between those obtained with Al_2O_3-SiO_2 and molybdenum catalysts, respectively.
7. From the experiments it may be concluded that it is possible by using different catalysts, to control the cyclic character of the products obtained by destructive hydrogenation of paraffin wax only within certain rather narrow limits. In all cases high pressure hydrogen appears to suppress cyclization to a considerable extent (compare results of a cracking experiment at 450°C in the absence of hydrogen [3]) ; even in the presence of specific cracking catalysts the average ring content of the reaction products never exceeds 0·2-0·4 rings per molecule.

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A graphical method of calculating ion-exchange processes*

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Summary—After briefly explaining the mathematical formulae which are used in the literature for studying front-shifting phenomena in a column with a solid adsorbent, the author describes a graphical method which is very closely related to the rectification diagram developed by McCABE-THIELE.

Although this graphical description only holds for continuous systems with a moving bed (and even then only approximately), it appears that good results can also be rapidly obtained when the ion-exchange is effected in fixed-bed columns. Loading and regeneration—two conceptions which are described in detail—yield various types of break-through curves : the stationary front curve and the front-widening curve.

A complete regeneration with an equivalent amount of regeneration agent may be carried out, *inter alia*, according to two operating lines i.e. in two steps separate by an additional operation. The loading may also be performed in two stages.

This graphical method has proved a great help in studying numerous applications of the process, some of which are briefly described.

Résumé—Après une courte explication des formules mathématiques, qui sont employées dans la littérature pour l'étude du déplacement du front dans une colonne contenant un adsorbant solide, l'auteur décrit une méthode graphique qui est intimement liée au diagramme de McCABE-THIELE pour la rectification.

Bien que cette méthode graphique porte uniquement sur des systèmes à écoulement continu de l'adsorbant solide, on a constaté qu'elle peut également conduire à de bons résultats pour l'échange d'ions dans les colonnes à lit fixe. La charge et la régénération—notions qui sont précisées—produisent différentes allures de déplacement du front : le front stationnaire et l'élargissement du front.

Une régénération complète avec une quantité équivalente d'agent de régénération peut se réaliser, entre autres, suivant deux lignes opératoires—c.à.d. en deux étapes—séparées par une opération additionelle. En outre, la charge peut s'effectuer également en deux étapes.

Comme caractéristique du processus, la méthode graphique s'est révélée un moyen utile pour l'étude de beaucoup d'applications de l'échange d'ions dont quelques-unes sont décrites sommairement dans cet article.

INTRODUCTION

In view of the great interest in ion-exchanging processes and the need for a deeper knowledge of what happens in the exchange column, many attempts have recently been made to find a mathematical solution of the problems which occur, especially, in chromatographic adsorption and ion-exchange processes performed in a fixed-bed column.

The approximation used in these attempts often renders the results unfit for use outside the laboratory, while the mathematical treatment has only led to a partial solution of the problems.

Hence it seemed desirable to make a search for new methods or analogies, giving a convenient survey of the possibilities offered by ion-exchange.

The method developed here is far from exact; nevertheless it clearly indicates what may be done with ion-exchangers.

After briefly explaining the mathematical treatment of the problem, and its limitations, we give an explanation of a graphical method which may be compared with known rectification theory.

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* Elaboration of a lecture read at the Symposium on ion-exchange at Breda on 24 January 1952.

MATHEMATICAL TREATMENT

If a solution containing a salt BZ is passed upwards at a given rate through a long column filled with a cation exchanger (AR), a break-through front will be formed, along which the concentration of the B-ions decreases in the direction of the current.

In general, the condition in the column at a given moment can be represented by the curves shown in Fig. 1. Below the point C, all of the exchanger has been converted into the B-state, so that the equivalent fraction $A/A + B$ in both the liquid (y) and the exchanger (x) is equal to zero.

The changes in value of the equivalent fractions in the exchanger and the solution are represented by curves r and s respectively.

The exchange takes place between C and D, i.e. along the entire frontier. Above D, the composition of the solution (y) as well as of the exchanger (x) is represented by the equivalent fraction $x = y = 1$. In chromatography a profound study has been made of the shape of this curve and of its shifting in the column. We are indebted, especially, to WILSON [1] and DON DE VAULT [2] for solving the first theoretical difficulties. As far as chromatographic adsorption is concerned, their theory may be described as follows :

Let us consider a column into which a solution is fed at the rate of V cc/sec. At a distance l from the inlet, the concentration of dissolved substance in the liquid is equal to c. At a distance $(l + dl)$ this concentration is $c + \left(\dfrac{\delta c}{\delta l}\right)_t dl$ (Fig. 2). The amount of dissolved material entering a given volume element of the column at a distance l from the inlet, is equal to $c \cdot V \cdot dt$.

The amount of liquid leaving this volume element is equal to $V dt$ and has a concentration of

Fig. 1. Diagram of the break-through curves obtained in reactions between the exchanger AR and dissolved BZ.

$c + \left(\dfrac{\delta c}{\delta l}\right)_t dl.$

The change in the amount of material is therefore given by $-\left(\dfrac{\delta c}{\delta l}\right)_t dl \cdot V \cdot dt$ and is equal to the change produced by the adsorption and to that brought about by the change in concentration of the liquid in the free space.

If Q represents the amount of adsorbed material per centimetre of column length, the change of Q in the volume element under consideration will be equal to

$$\left(\frac{\delta Q}{\delta t}\right)_l dt \cdot dl .$$

The change in the amount of material in the free space is $\alpha \left(\dfrac{\delta c}{\delta t}\right)_l dt \cdot dl$, where α is the free space per centimetre of column length. The differential equation (material balance) following from the above is :

$$\left(\frac{\delta c}{\delta l}\right)_t dl \cdot V \cdot dt + \alpha \left(\frac{\delta c}{\delta t}\right)_l dl \cdot dt + \left(\frac{\delta Q}{\delta t}\right)_l dl \cdot dt = 0$$

or :

$$V \left(\frac{\delta c}{\delta l}\right)_t + \alpha \left(\frac{\delta c}{\delta t}\right)_l + \left(\frac{\delta Q}{\delta t}\right)_l = 0.$$

Assuming that the equilibrium between the adsorbent and the solution is directly established, this equation leads to a simple result.

For $Q = Mf(c)$

or :

$$V \left(\frac{\delta c}{\delta l}\right)_t + \alpha \left(\frac{\delta c}{\delta t}\right)_l + M \cdot f'(c)\left(\frac{\delta c}{\delta t}\right)_l = 0$$

$$V \left(\frac{\delta c}{\delta l}\right)_t + \{\alpha + M \cdot f'(c)\}\left(\frac{\delta c}{\delta t}\right)_l = 0$$
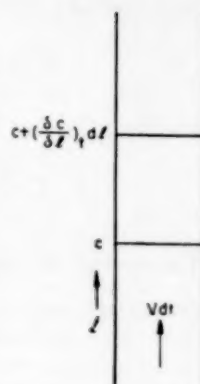

Fig. 2. Volume element in the column at a distance l from the inlet.

substitution of :

$$- \left(\frac{\delta t}{\delta l} \right)_c \left(\frac{\delta c}{\delta t} \right)_l = \left(\frac{\delta c}{\delta l} \right)_t$$

yields the following equation :

$$\left(\frac{\delta l}{\delta t} \right)_c = \frac{V}{\alpha + M \cdot f'(c)}$$

$\left(\frac{\delta l}{\delta t} \right)_c$ represents the rate at which a point on the break-through curve of a constant concentration c travels through the column. In this case there are two solutions for the rate equation which depend upon the nature of the adsorption equilibrium.

If the quantity $\frac{d \, M f(c)}{dc}$ as a function of c decreases continuously, a clear-cut horizontal break-through front is formed ; if, however, it increases with the concentration, the length of the break-through front will increase.

If the equilibrium is not directly established, the clear-cut horizontal front will be changed into a stationary front which extends into the column to a depth depending among other things upon the flow-rate of the liquid. The extent of the front-widening is at first enlarged by the non-instantaneous establishment of the equilibrium.

When applied to ion-exchange, these results provide the following picture :

If in a column an ion-exchanger, loaded with one type of ion, is traversed by a flowing solution containing another type of ion, a clear-cut break-through front will occur if the new ion is more strongly adsorbed than the old, whereas if the new ion is less strongly adsorbed than the old there will be formed a front of ever-increasing length. The mathematical formulae to give a rapid and quantitative solution of the case in which equilibrium is directly established become very involved when applied to those cases in which the reaction proceeds at a finite velocity. It should be remarked, however, that we do not know much about the velocity at which ion-exchange processes proceed in concentrated solutions.

Nevertheless repeated attempts have been made to integrate the differential equation involved, not only in the cases where equilibrium obtains, but also in those cases where the exchange does not momentarily lead to an equilibrium.

THOMAS [3] and WALTER [4] looked upon the exchange as a chemical reaction ; they consequently assumed that the reaction, following the law of mass action, proceeds slowly in comparison with the diffusion. As the rate-determining factor BOYD et al. [5] adopted the diffusion in the liquid film around the grain.

However, considerations based upon the diffusion in the exchanger gel may equally well be put forward, the more so as a recent publication by BOYD et al. [6]. has shown that, in many reactions in a more strongly concentrated medium, this interior diffusion may be the rate-determining factor.

In all these cases, however, a quantitative solution of the formulae is a very intricate operation and often, in practice, impossible. Consequently, we have to content ourselves with the qualitative results i.e. *the stationary front* and *the front-widening*. In many cases it will be necessary for us to know more about the actual shape of the break-through curve. This is the reason why we have resorted to another way of solving the problem. The fact that the mathematical method gives a description of the front-widening, without providing a means for eliminating this front-widening, is a strong argument for seeking a better solution.

GRAPHICAL TREATMENT

In 1931 AUSTERWEIL [7] compared the ion-exchange to a discontinuously performed extraction and derived simple mathematical formulae for this process.

MARTIN AND SYNGE [8] drew a parallel between partition chromatography and rectification. By adopting a linear partition isotherm and introducing the conception of a " theoretical plate " they calculated the number of theoretical plates needed for a given separation.

But it is not possible to develop an entirely satisfactory explanation of the process on the basis of this theory.

The close resemblance that the ion-exchange

process shows to the well-known counter-current operations demands a more detailed elaboration of the parallel with the rectification process, described by means of diagrams in which equilibrium lines and operating lines can be drawn.

The graphical methods commonly applied to rectification are those developed by PONCHON-SAVARIT and by McCABE-THIELE.

In what follows we shall only deal with the latter method since, generally speaking, it is easier to apply than the former and, in the case of ion-exchange, easier to describe.

LOADING OF THE ION-EXCHANGER

By the term loading we mean the reaction between the exchanger and a solution containing an ion which in all equivalent fractions is more strongly bound by the exchanger than the ion originally present on the exchanger.

Instead of allowing the break-through curve to move along the ion-exchanger in the column, we consider a column to which exchanger (AR) and solution (BZ) are fed into counter-current in such a way as to establish a stationary
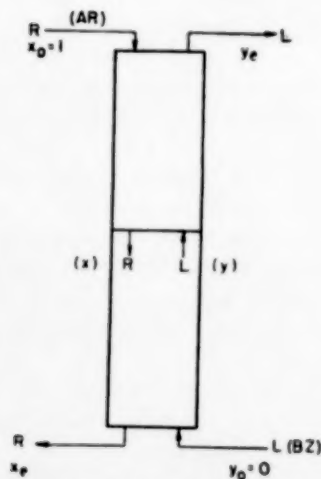
Fig. 3. Column into which R equivalents of AR and L equivalents of dissolved BZ are continuously fed per unit time.

condition in the column. Into the top of the column R equivalents of exchanger are fed per unit time. The equivalent fraction is :

$$x_o = \frac{A}{A + B} = 1$$

These R equivalents of exchanger move through the column ; at the base of the column R equivalents of exchanger leave with an equivalent fraction of x_e.

Per unit time, L equivalents of BZ (in solution) are supplied to the base of the column ; equivalent fraction

$$y_o = \frac{A}{A + B} = 0.$$

From the top of the column are discharged L equivalents of $AZ + BZ$; equivalent fraction y_e.

The material balance for the entire column is therefore :

$$Rx_o + Ly_o = Rx_e + Ly_e$$

or :

$$R = Rx_e + Ly_e \qquad (1)$$

The material balance for the upper part of the column is :

$$Rx_o + Ly = Rx + Ly_e \text{ or as } x_o = 1$$

$$y = \frac{Rx}{L} + \left(y_e - \frac{R}{L}\right). \qquad (2)$$

The latter equation represents the formula of the operating line and denotes the relationship between x and y in a given horizontal section. An objection which may be raised against the foregoing is that the amount of $(AZ + BZ)$ rising through the column is not equal at all points, since the exchanger is a gel and will consequently absorb an amount of AZ and BZ which is not negligible. This is why the exchanger discharged from the base of the column contains some BZ.

This objection may be obviated by plotting curved operating lines or by making use of another graphical method, e.g. the method developed by PONCHON-SAVARIT. The objection ceases to exist if the concentration of the solution is low. The amount of electrolyte absorbed in the gel may then be neglected. The formulae (1) and (2) are applied to the reaction :

$$AR + BZ \rightarrow BR + AZ.$$

From this equation it appears that for a quantitative conversion it is desirable to equalize the quantities R and L. Consequently formula (1) becomes :

$$1 = x_e + y_e$$

and formula (2) :

$$y = x + (y_e - 1) \text{ or } y = x - x_e.$$

Fig. 4 shows the equilibrium line for the loading process. As the affinity of the exchanger for B-ions is greater than for A-ions, the $\dfrac{A}{A+B}$ fraction in the solution will be greater than in the exchanger. The equilibrium curve consequently lies above the diagonal. For the value $x = 1$ the operating line

$$y = x + (y_e - 1)$$

intercepts a length (y_e) on the side of the rectangle

$$(0 < y_e < 1) \,.$$

From the figure it appears that for a conversion, as illustrated here, where a liquid is produced with an equivalent fraction y_e and an exchanger with an equivalent fraction x_e, it
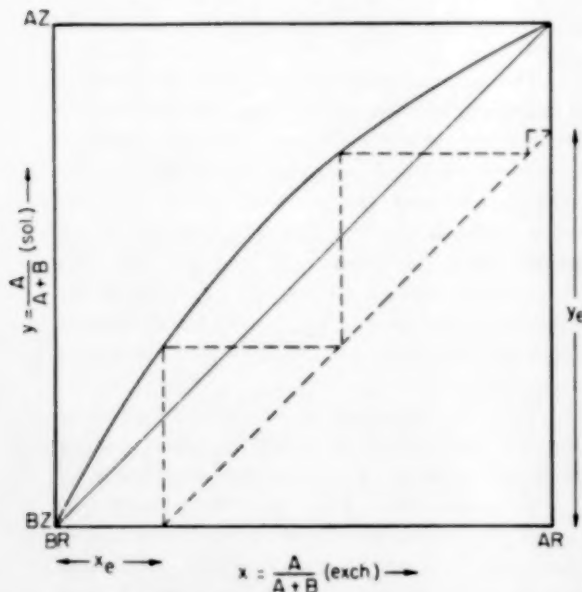
Fig. 4. Equilibrium curve for the process of loading AR with a BZ-solution, and an operating line which by shifting can be made to coincide with the diagonal.

suffices to use a small number of theoretical plates.

If, however, we shift the operating line until it approaches very close to the diagonal, which is allowable, the issuing liquid consists of practically pure AZ ($y_e = 1$), while the exchanger, leaving from the base of the column, consists of practically pure BR ($x_e = 0$).

From the diagram it appears that in this case we need more theoretical plates, and are therefore obliged to use a much longer column (all other conditions remaining unchanged).

The entire stationary break-through curve in the moving-bed column is maintained.

Loading carried out in a fixed bed

This approach may also be applied to the fixed-bed process, the only difference being the fact that we are now compelled to supply such an additional amount of BZ-solution to the lower part of the column as is needed to fill the free space in that part of the column where all exchanger has been converted into the B-state.

During a loading process performed in an infinitely long column we consequently always get a stationary break-through curve. In the case where loading is performed in a series of fixed-bed columns we may also obtain a stationary condition. In this case a BZ-solution is continuously fed into the *first* column and an AZ-solution is drained from the *last* column, by arranging that once per period—i.e. the time needed for shifting the break-through curve over one column length—a fully loaded column is disconnected from the front of the series while a fully regenerated and washed column (AR) is connected to the end.

Hence, it is evident that in this case the amount of ion-exchanger (in equivalents) which is connected in every period to the end of the series of columns will be smaller than the amount of solution (in equivalents) fed into the first column, since at the moment when the fully loaded column is disconnected the free space in that column is entirely filled with BZ-solution.

Summarizing, we arrive at the conclusion that if loading is performed in an infinitely long column there will always be formed a complete

and stationary break-through curve. In a moving bed and in a series of fixed-bed columns to which and from which columns are regularly connected or disconnected, a stationary condition will be established, although this does not necessarily imply that the conversion will be a complete one. It is, however, also possible to attain complete conversion in these cases.

REGENERATION OF THE ION-EXCHANGER

Regeneration by which term we mean the reaction between the exchanger and a solution containing an ion which for all equivalent fractions is less strongly bound than the ion originally present on the exchanger, may be studied in the same way.

During the regeneration of BR in a moving bed by means of an AZ-solution, the diagram shown in Fig. 5 is obtained. In this case, however, the equilibrium curve lies below the diagonal. For the case $R = L$ the operating line $y = \dfrac{R}{L} x + \left(y_e - \dfrac{R}{L} \right)$ will intercept a length y_e on the axis $x = 1$ as shown in Fig. 5.

As in a stationary case the operating line cannot intersect the equilibrium curve, the operat-

ing line cannot be shifted so as to make it coincide with the diagonal. If, however, use is made of an excess of regenerating agent ($L > R$) it will be possible to operate according to an operating line W_2 passing through the point $x = 0$ and $y = 0$. In this case, therefore, a fully regenerated exchanger is formed, while the outgoing liquid contains both AZ and BZ. At the same time Fig. 5 shows that regeneration carried out with a deficiency of regenerating agent is possible; in this case the operating line (W_3) passes through the point $x = 1$ and $y = 1$. Here, a liquid is formed containing BZ only, the exchanger being only partially regenerated. Summarizing, we may say that when BR is regenerated with AZ according to one operating line the following three mixtures may be formed :
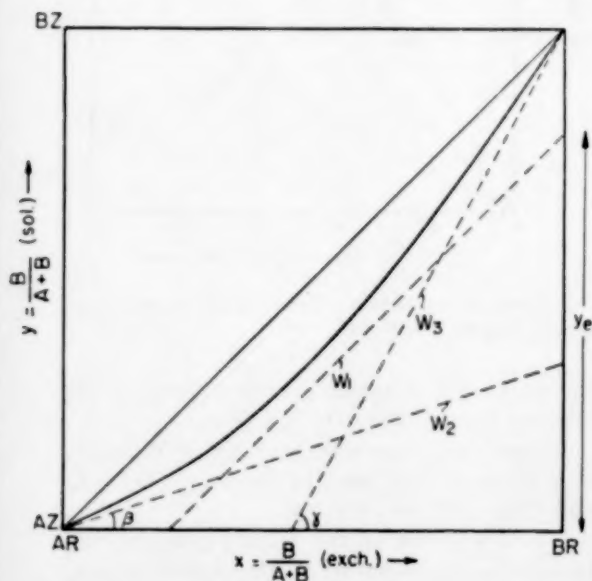
(1) a mixture of dissolved AZ and BZ alongside pure AR (operating line through $x = 0$ and $y = 0$);

(2) a mixture of AR and BR and dissolved BZ (operating line through $x = 1$ and $y = 1$);

(3) a mixture of dissolved AZ and BZ alongside a mixture of AR and BR.

Consequently it will be seen that during regeneration it is not possible to convert simultaneously all BR into AR and all AZ into BZ.

Regeneration carried out in a fixed bed

Here, too, it is possible to change over from the continuous moving bed to the fixed-bed column process.

A pure AZ-solution is fed continuously into the first of a series of columns and a solution containing both AZ and BZ is discharged from the last column, while once in every period a fully loaded column is connected to and a fully regenerated column disconnected from the system. This operation, carried out with an excess of regenerating agent, is represented by the operating line W_2. As this operating procedure it is not entirely continuous, the solution of (AZ and BZ) produced per period is not constant in composition. The terminal point of the operating line gives the average composition of the resulting solution.

The smallest excess of regenerating agent

Fig. 5. Equilibrium curve for the regeneration of BR with AZ-solution. The operating line W_2 denotes the total regeneration carried out with an excess of AZ-solution.

required for effecting a complete regeneration is indicated by the tangent through the point $x = 0$, $y = 0$ to the equilibrium curve $\left(\tan \beta = \dfrac{R}{L} \text{ must be a maximum}\right)$.

When operating according to the line W_3 shown in Fig. 5, where the regeneration is carried out by adding a pure AZ-solution to the first column of a series and by discharging a pure BZ-solution from the last column, the composition of the regenerated column will not be uniform throughout the column.

The point of intersection between the operating line W_3 and the abscissa AR–BR gives the mean composition of the regenerated column. In a regeneration of this type the aim is to make the amount of regenerated product as large as possible. It follows that the angle included between the line W_3 and the axis AR–BR, which is a measure of the deficiency of regenerating agent applied, must be made as small as possible. The smallest angle possible is obtained by plotting the tangent to the equilibrium curve through the point $x = 1$, $y = 1$

$$\left(\tan \gamma = \frac{R}{L} \text{ must be a minimum}\right).$$

In many cases (e.g. with uni-divalent systems), however, the equilibrium curve may be shifted by varying the total electrolyte concentration in the solution. For example, the Ca-H-equilibrium curve for a strongly acid exchanger (say Dowex-50), which in a very dilute solution is remotely distant from the diagonal (very high affinity of the exchanger to the Ca-ions), can be shifted towards the diagonal by increasing the concentration (BAUMAN and EICHHORN [9]).

By raising the concentration in these cases it is possible, therefore, to enlarge the angle included between the axis AR–BR and the tangent through the point $x = 0$, $y = 0$ to the equilibrium curve, as well as to reduce the angle included between the axis and the tangent through the point $x = 1$, $y = 1$ to the equilibrium curve.

An increase of the former angle β implies that the complete regeneration may be carried out with a smaller excess of AZ.

A reduction of the latter angle γ implies that the partial regeneration of the exchanger in which the regeneration agent is entirely consumed will be more complete.

For these reasons it will be clear that an equilibrium curve which can be shifted to within a short distance from the diagonal is favourable for regeneration.

In the application of strongly alkaline exchangers, it is possible in some cases, by varying the concentration, to shift an equilibrium curve so far that the affinity gets reversed. For example, the Dowex-2 exchanger, when supplied to solutions containing 50 m.eq. CO_3'' and OH' in all per litre, shows a strong affinity to the CO_3''-ion. If the concentration of the solution is raised to 1000 m.eq. CO_3'' and OH' per litre,
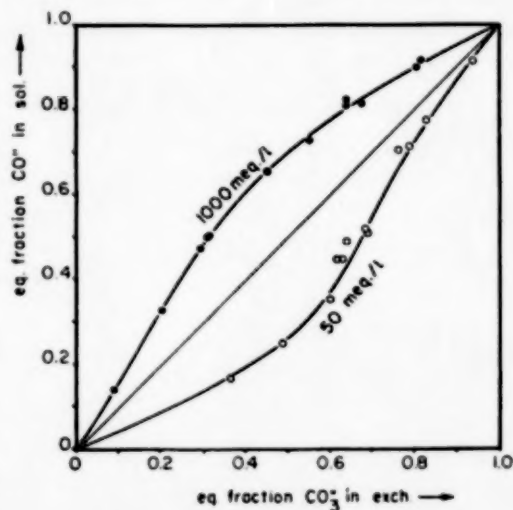

Fig. 6. Equilibria between Dowex-2 and solutions containing Na_2CO_3 and NaOH.

the exchanger shows a greater affinity to the OH'-ion than to the CO_3''-ion (Fig. 6).

Similar phenomena were described by WHEATON and BAUMAN [10] for the systems $SO_4'' - Cl'$ and $CO_3'' - Cl'$ on Dowex-2.

This reversal of the affinity may be very favourable as, according to the definition given for the loading, both the removal of CO_3''-ions from very dilute solutions by means of Dowex-2-OH and the conversion of Dowex-2-CO_3'' into

the OH-state by means of a 1 norm. NaOH-solution must be considered as loading processes. This means that both operations can be carried out with equivalent amounts of exchanger and electrolyte solution.

PROCESS ACCORDING TO TWO OPERATING LINES

Although this operating-line theory gives us a further insight into the ion-exchange process, it leads, in its simple form to few, if any, new results. Irrespective of the fact that practically all operations suggested before were carried out in one column, so that there was no question of a continuous process, all of these loadings and regenerations might be described with one operating line.

However, the theory developed here makes possible the working of a continuously-running exchange process with equivalent quantities of material [12].
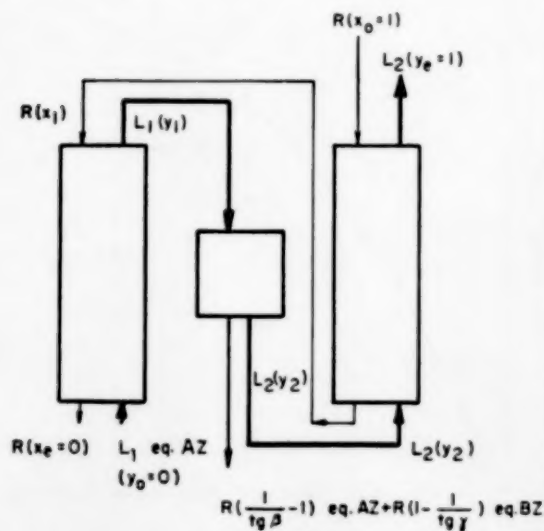
Fig. 7a. Diagram for regeneration carried out in two stages.

We succeeded in working such a process *by performing the regeneration according to two operating lines.*

For a moving-bed system this may be explained in the following way (Figs. 7a and 7b).

The first part of the regeneration takes place
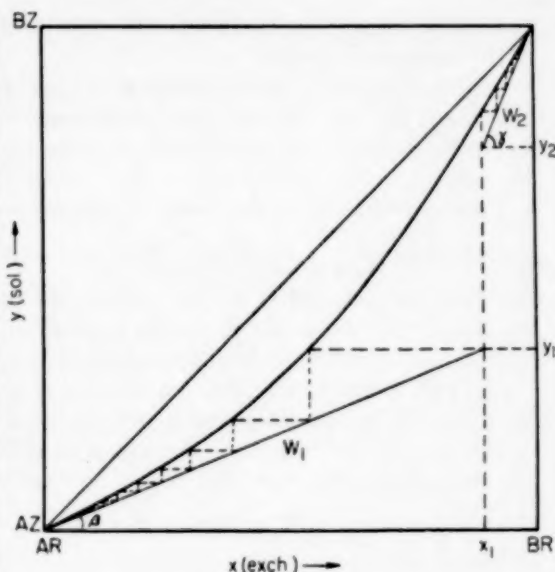
Fig. 7b. Regeneration carried out according to two operating lines.

in a column to which R equivalents of exchanger (having a composition x_1) and L_1 equivalents of solution ($y_o = 0$) were supplied per unit time (first operating line).

The material balance for the column is

$$Rx_1 + L_1 y_o = Rx_e + L_1 y_1$$

or as $x_e = 0$ and $y_o = 0$:

$$Rx_1 = L_1 y_1.$$

The liquid issuing from this column (L_1 equivalents, having a composition y_1) is subjected to an additional treatment in order to free it of a part of the dissolved material, as a result of which the composition of the solution adopts the value y_2.

The resultant solution (L_2 eq. composition y_2) is fed into the second column and contacted in counter-current with R equivalents of exchanger ($x_o = 1$) (second operating line). As $x_o = 1$ and $y_e = 1$, the material balance for this column reads :

$$R + L_2 y_2 = L_2 + Rx_1.$$

Simple formulae give the relationship between the amount to be removed between the two

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exchanger treatments and the direction coefficient of the two operating lines.

In the ideal case it will be necessary to remove —between the two operating-line treatments— the entire excess of AZ used for the regeneration $(L_1 - R)$ eq.

Since $\tan \beta = R/L_1$, it is necessary, therefore, to remove $R\left(\dfrac{1}{\tan \beta} - 1\right)$ eq. AZ. However, after the treatment according to the first operating line a small amount of BZ must also be removed from the solution. This is due to the fact that the second operating line does not coincide with the diagonal ; in case these lines should coincide, it will be sufficient to remove the excess of AZ.

As regards BZ there has to be removed :

$$Rx_o + L_1 y_o - Rx_e - L_2 y_e = R - L_2$$

and since

$$\tan \gamma = \frac{R}{L_2}$$

$$R\left(1 - \frac{1}{\tan \gamma}\right) \text{ eq. of } BZ.$$

γ represents the angle included between the second operating line and the axis AR–BR.

If in the regeneration we should allow a small loss of AZ, it suffices to remove almost the entire excess of AZ, between the two operating line treatments ; the course of the equilibrium curve being as shown, the second operating line cannot possibly pass through the point $x = 1$, $y = 1$, but will cut the axis $x = 1$ at a lower point so that after the second operating line the solution will contain a small amount of AZ alongside a large amount of BZ.

In this case the slope of the second operating line will be smaller than $45°$.

This result (the conversion with equivalent amounts of material) which can be obtained by carrying out the regeneration according to two operating lines, can also be obtained in the following way. A partial regeneration may be superseded by a loading according to two operating lines (Figs. 8a and b).

In the second column, the exchanger having a composition x_2 is traversed by a liquid having the composition y_1 (or y'_1) (second operating line). As a result an exchanger is formed having the
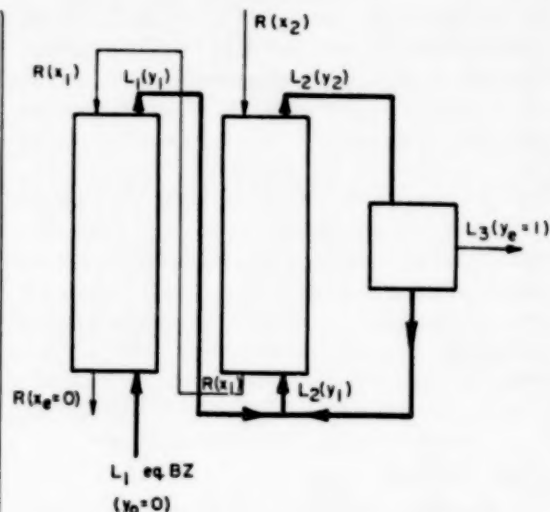

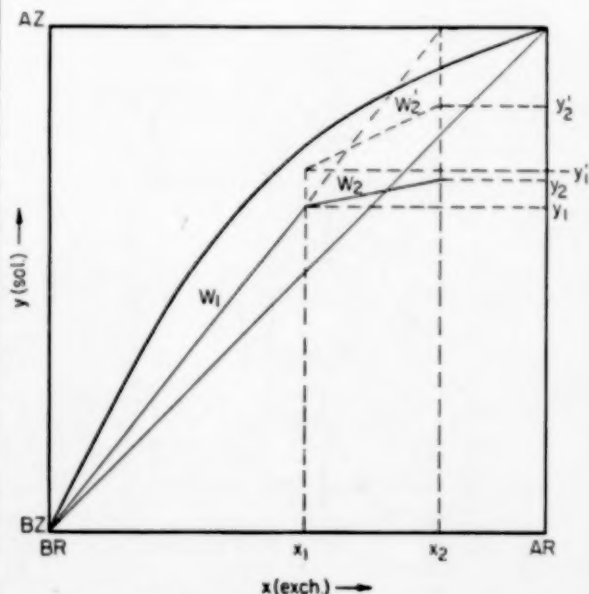Fig. 8a. Diagram of a loading process carried out in two stages.

Fig. 8b. Loading process performed according to two operating lines.

composition x_1 and a solution having a composition y_2 (or y'_2). In the first column, the exchanger (x_1) is traversed by a pure BZ-solution $(y_o = 0)$ which leads to the formation of a fully loaded exchanger BR $(x_e = 0)$ and a solution of the composition y_1 (first operating line).

In the application of this method an additional treatment will be needed after the second operating line treatment. When following the above procedure it is not necessary for the starting point of the second operating line (W_2) to coincide with the terminal point of the first (W_1), only the x_1-value must be equal for these points. The slope of the first operating line is such that the line, where produced, intersects the axis $y = 1$ at the point x_2.

This point x_2 denotes the composition of the regenerated exchanger added. The x-value of the terminal point of the second operating line $(W_2$ or $W'_2)$ is consequently equal to x_2.

As an additional treatment for effecting a change in the composition of the solution there may be considered, for example, a distillation, an extraction or a crystallization.

Process according to two operating lines in fixed-bed columns

In these processes where the regeneration or the loading is carried out according to two operating lines, we may use two series of columns instead of two columns with a moving bed.

Now the terminal point of the first operating line and the starting point of the second operating line only hold for the gross composition of the exchanger of the entire column and for the gross composition of the solution produced per period.

The lack in complete continuity is the reason why there will occur a great fluctuation in composition (especially in the liquid produced according to operating line 1), which may vary during the regeneration effected in one period from a value differing only slightly from y_2 to a value approaching zero.

The degree of this fluctuation depends, amongst other things, on the length of the column which is connected to the system in each period.

While a column is being switched over from one operating line to the other, this column is not washed.

It will be clear that in this case the application of the operating-line construction is somewhat forced. As a matter of fact this was to be expected since this operation does not proceed continuously but only semi-continuously.

AZEOTROPY

The reversal of the affinity caused by a change in the total concentration of the electroyte in the solution has already been mentioned (Fig. 6).

There is also another type of affinity-reversal, caused by a change in the equivalent fraction in the solution.

This so-called adsorption-azeotropy occurs with the strongly alkaline exchangers on a quaternary ammonium basis. Fig. 9 shows the equilbrium curve for OH'-ions and Cl'-ions on Dowex-2 (temperature 20°C and 50 m.eq. OH + Cl/1 ; see also WHEATON and BAUMAN [10]).
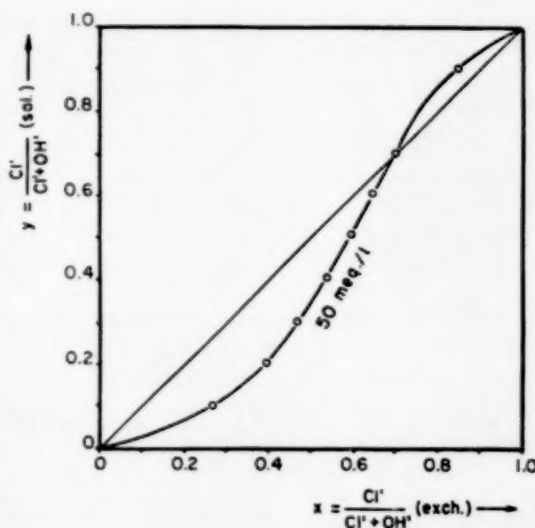

Fig. 9. Equilibria between Dowex-2 and solutions containing NaCl and NaOH.

In this case a front-widening will occur both in the reaction of Dowex-2-OH with NaCl and in the reaction of Dowex-2-Cl with NaOH carried out in an infinitely long column.

According to the definition used by us these procedures cannot be considered as a loading nor as a regeneration, as the definition implies that the affinity is the same for all equivalent fractions.

However, the occurrence of a front-widening is the reason why this reaction may best be considered as a regeneration.

WASHING OF THE ION-EXCHANGER

As the exchanger is a gel, it will invariably absorb a certain amount of the dissolved material. After loading and regenerating this amount of material must be washed out of the gel before the following treatment can be undertaken. If washing is performed as a continuous operation in a moving bed, formulae may be derived for this process which are analogous to the formulae applied in the loading process.

R equivalents of exchanger, in which one electrolyte has been absorbed in the gel-phase, are continuously supplied to the top of the column. The concentration of absorbed material amounts to p_o eq. per 1 eq. of exchanger. The product issuing at the base of the column has been thoroughly washed ($p_e = 0$).

In counter-current to the outgoing flow, S litres of water ($q_o = 0$) are supplied to the base of the column and discharged through the top. On leaving the column, this water contains q_e eq. of electrolyte per litre. Now the material balance for the entire column reads :

$$Rp_o = Sq_e.$$

For the upper part of the column, the following equation holds :

$$Rp_o + Sq = Rp + Sq_e$$

from which the formula for the operating line W can be derived :

$$q = \frac{R}{S}p + \left(q_e - \frac{R}{S}p_o\right),$$

in which formula q and p stand for the amount of electrolyte in a horizontal cross section in the solution and in the exchanger, respectively.

As $Rp_o = Sq_e$, the formula for the operating line consequently becomes :

$$q = \frac{R}{S}p.$$

The operating line W describing this process will pass through the origin of the plot.

The graphical representation is shown in Fig. 10. q represents the amount of electrolyte present in the solution (eq./1). p stands for the amount of electrolyte in the gel phase (eq. electrolyte/eq. exchanger).
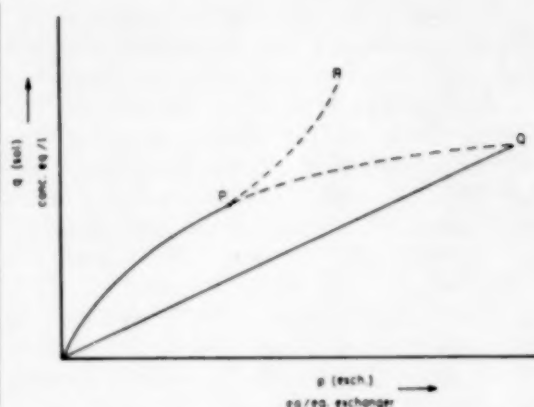

Fig. 10. Equilibria between exchanger gel and the surrounding liquid which contains one dissolved substance.

An obvious shape of the equilibrium curve is the one for which the concentration in the solution (for small values) is greater than the concentration in the gel phase.

Little can be said, as a rule, about the deviation PQ or PR. But in the systems investigated by us we have found that the deviation of the equilibrium curve always occurs according to PQ, which implies that by the washing treatment a solution can be obtained which possesses the original concentration. It will be clear, therefore, that in an infinitely long column a stationary front will be formed along which the concentration of the dissolved material increases in the direction of the liquid current.

Hence this front is exactly comparable with the front formed during the loading treatment. This stationary condition can also be realized in a series of columns from the last one of which a solution is obtained having the same concentration as the solution with which the loading or regeneration had been effected.

APPLICATIONS

Only brief outlines can be given here of a few processes to which this study of the operating lines can be applied. A quantitative elaboration would require an extensive knowledge of the height corresponding to one theoretical plate (H.E.T.P.), and be outside the scope of this article.

However, the conclusions drawn for continuous systems may in many cases be applied qualitatively to fixed-bed, single column processes.

The loading process offers only few points of interest, since dilute solutions are generally used. In these cases, the height of the column corresponding to one theoretical plate is small, so that the exchange will take place only over comparatively small height. The practically horizontal front offers few difficulties. When applied to regeneration, where a front-widening occurs, this graphical method may lead to a clearer understanding of the process. As was

When the regeneration is performed in a column with a fixed bed, the concentration of the regeneration agent is again of great importance. To study the effect of this regeneration, tests were made in a column with a 100-cm deep bed filled with Dowex-50. Across this column, loaded with Ca++, HCl solutions of different concentrations were passed at a known rate. From analyses of the successive eluants, calculations were made of the amount of exchanger regenerated at a given moment and the efficiency of the regeneration agent used. These data are broadly represented in Fig. 12 for three concentrations
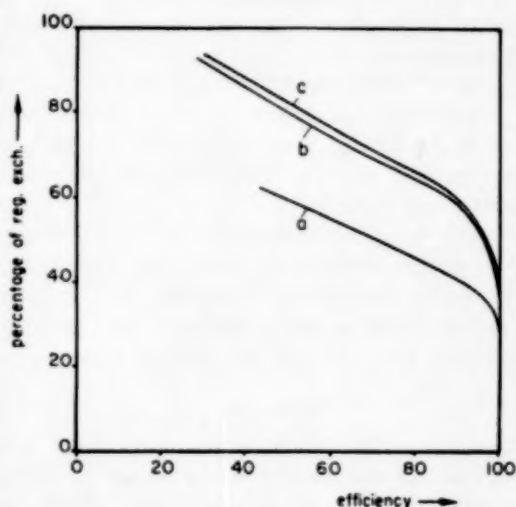

Fig. 11. Equilibria for Ca++ and H+ between Dowex-50 and solutions of a fluctuating concentration (1000-1500-3000 m.eq./1).

Fig. 12. Relation between the percentage of regenerated product and the efficiency of the regeneration (Ca-Dowex- + HCl).

stated before the equilibrium curve of the " Ca++ — H+ on Dowex-50 "-system is highly dependent on the concentration in the solution. As the tangent through the point $x = 0$, $y = 0$ to the equilibrium curve is a determining factor for the minimum excess needed in the continuous performance of a total regeneration, the location of this equilibrium curve will be of great importance.

Fig. 11 shows some equilibrium curves between Dowex-50 and solutions with varying Ca++ — H+ concentrations (1000–1500 and 3000 m.eq./1).

of the regenerating agent : curve a for 1 N, curve b for 2 N and curve c for 3,5 N hydrochloric acid. Although the difference between the lines for the 1 and 2 N solutions is relatively great, that between the lines for the 2 and 3,5 N solutions is much smaller. This is due to the fact that the angle included between the tangent and the abscissa increases less rapidly with change in the concentration when the concentration in the solution is already high, as well as to the fact that a discontinuous system was being used here instead of a continuous system. Consequently the theoretical plates number of the column will

be smaller according as the concentration in the solution is higher, with the result that at high concentrations the column will operate less efficiently. At an increase in concentration, this latter phenomenon might even lead to a decrease in regenerating efficiency.

However, if a 3,5 N HCl solution is used instead of a 2 N solution, the efficiency at a given percentage of regenerated material will be greater, as could be expected from the location of the equilibrium curve.

Further elaboration of these data cannot be made here.

Double conversion processes form another field of application. The use of ion-exchangers for carrying out double conversions was suggested long ago. Details can be found in various patents registered in the names of AUSTERWEIL [11] and Norsk Hydro [11]. It is even possible to manufacture $NaNO_3$ from $Ca(NO_3)_2$ and sea-water along these lines.

The very first ideas were based on the use of a column which was alternately loaded and regenerated in opposite directions. In this case also, the use of operating lines may be a welcome expedient for analysing the process.

CONCLUSION

It has been shown that the use of operating lines may be valuable in the study of the problems occurring in ion-exchange processes. Just like the mathematical treatment, the construction of the operating line clearly proves that, in the course of the loading process performed in an infinitely long column, there will occur a front-widening.

During the complete regeneration, however, a continuous condition can be established by obtaining a liquid in which the regenerating agent has been only partly used.

The use of two operating lines in the regeneration or the loading process has proved to be very helpful. It makes possible the exchange of ions in equivalent amounts. In many cases the ion-exchange as such will not be capable of providing a complete solution of the problem, so that it will be necessary to perform an additional operation.

It has been impossible to give here a complete description of the practical application of two operating lines. This point will be the subject of a future publication.

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NOTATION

AR = exchanger loaded with A-ions
BZ = dissolved electrolyte with B^+-cations
y = equivalent fraction in the solution
x = equivalent fraction in the exchanger
r = break-through curve for the ion-exchanger
s = break-through curve for the solution
V = amount of solution added to the column (cc/sec)
l = distance from the column inlet
c = concentration of the material dissolved in the liquid
t = time in sec
Q = amount of adsorbed material per cm of column length
α = free-space per cm of column length
R = number of equivalents of exchanger supplied per unit time
L = number of equivalents of dissolved electrolyte supplied per unit time
x_0 = equivalent fraction in the exchanger at the inlet of the column
y_0 = equivalent fraction in the solution at the inlet of the column

x_e = equivalent fraction in the exchanger at the outlet of the column

y_e = equivalent fraction in the solution at the outlet of the column

β, γ = angles included between the operating line and the abscissa

S = amount of water (in 1) supplied during the washing process per unit time

p = amount of electrolyte in the gel phase (in eq. per eq. of exchanger)

q = concentration of the electrolyte in the washing water (eq./1)

W = operating line

Stabilizing effects in compressible filter cakes

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Summary—The filtration of polyvinyl chloride particles of 5-12 in water has been investigated under constant pressure and constant rate conditions. The porosity of the cake was measured at different levels by means of the electrical resistance between gauge pins.

A form of ' retarted packing compressibility ' has been found in which the first layers of cake do not compress gradually but only after a critical cake thickness has been reached. This critical cake thickness can be reduced by the addition of a deflocculant.

Résumé—Dans une introduction sommaire, l'auteur explique la cause de la compression qui se produit dans les différentes couches d'un tourteau de filtration et décrit l'appareil employé pour ses mesures. Il discute un phénomène observé pendant la filtration de suspensions aqueuses de chlorure de polyvinyle.

Se basant sur la distribution de la pression et de la porosité dans les tourteaux et sur les changements de la vitesse de filtration en fonction de l'épaisseur du tourteau, l'auteur arrive à la conclusion que le phénomène résulte d'une compression de la structure du tourteau qui, lorsque ce dernier a atteint une épaisseur critique, ne se produit que dans une couche de fond d'épaisseur croissante. La couche supérieure a une plus grande porosité ; elle est probablement stabilisée par des effets électroniques.

1. Introduction

In theories of cake filtration it is usual to distinguish between compressible and non-compressible filter cakes. Non-compressible cakes are defined as cakes of which the mean specific resistance does not vary with the filtration pressure. All other cakes are called compressible.

We will here deal with cakes which, when of small thickness, were found to be non-compressible but which proved to be compressible at greater thicknesses.

It is well known that in compressible filter cakes the lower cake layers are more compressed than the higher ones. This is caused by the cake pressure, which increases from top to bottom.

Throughout the cake the sum of cake pressure and liquid pressure is constant and equal to the liquid pressure above the cake.

This cake pressure must be distinguished from the particle pressure, which term is often used wrongly in the literature for what we call cake pressure.[*]

In a study on the cake structure it is as well to know the cake pressure at any point in the cake. Since this cake pressure can be derived at once from the liquid pressure, the distribution of the liquid

pressure throughout the cake can be measured instead.

The apparatus, described in the next section was used for this purpose.

2. Description of Apparatus Used

With reference to Fig. 1 a short description of this apparatus will be given. Its principal parts are : the filter proper (3), the supply vessel for filtration at constant rate (5), the supply vessel for filtration at constant pressure (1), a manometer panel (2), and a buffer vessel (6). The whole apparatus is made of brass in order to avoid corrosion. The pressure in the supply vessel for constant pressure is controlled by the reducing valve (7) and can be read from the manometer (8a).

The supply vessel for filtration at a constant rate contains a plunger, which can be pressed downwards at a constant rate by a long worm gear and gear wheels, by means of which the rate can be changed. The plunger presses the slurry ahead of it through the filter and at the same time the pressure difference along the filter rises. The slurry is recycled through pipe D from the filter via a circulating pump back to the supply vessel used to avoid settling in the pipes.

The filter itself consists of a cylindrical vessel with a cross section of 100 cm², a content of 1·6 litres and is vertically assembled. The filter vessel is provided

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[*] In a future paper these terms will be discussed more thoroughly.
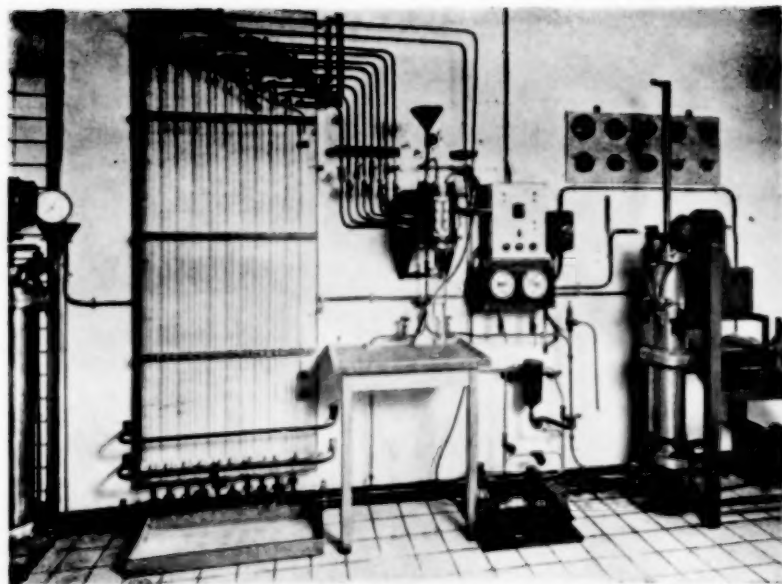
Fig. 2.   Apparatus for filtration experiments at constant pressure and constant velocity (complete assembly).
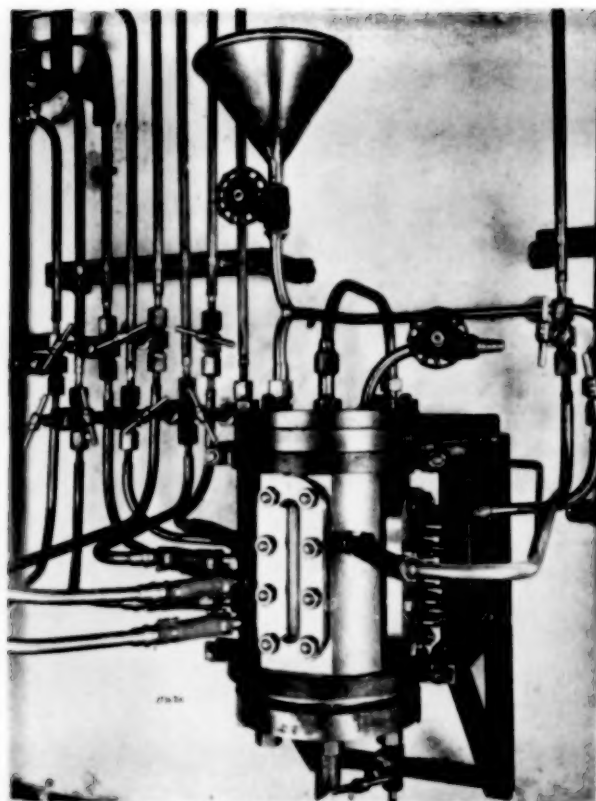
Fig. 3. Filtration apparatus detailed filter head with manometer
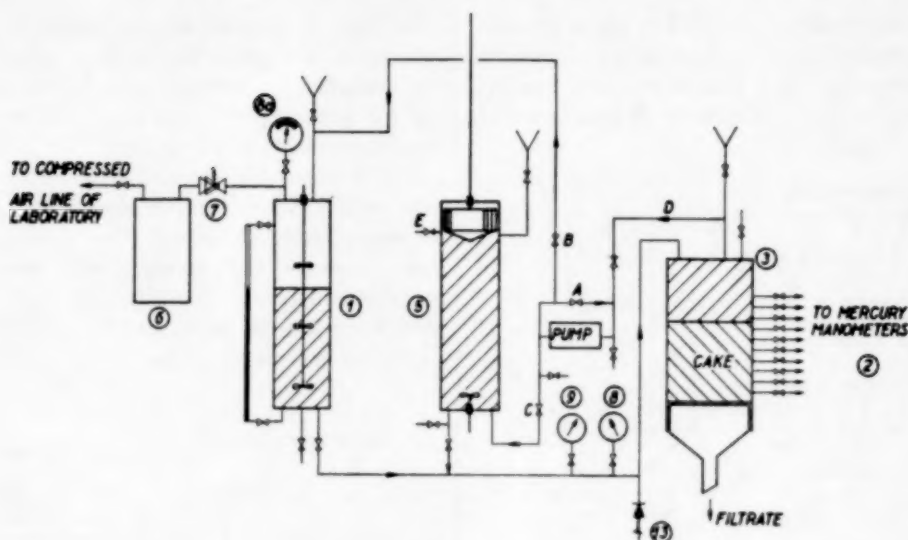connections, etc.

Fig. 1

with two opposite sight glasses, one of them being calibrated in centimetres to measure the cake thickness.

Metal pins are inserted into the cake at different levels ; these pins are assembled on a plate of insulating material for which an opening is left in the side of the filter vessel. The purpose of these pins is to measure the electric resistance in the cake. If they are left in position, the cake removed and the filter vessel filled with the filtrate, the electrical resistance can again be measured. By dividing the first resistance by the second a dimensionless quantity λ/ϵ is found in which ϵ is the porosity and λ the tortuosity factor. If the pores in the cake are straight, of equal diameter and parallel to the direction of the electrical field this quotient would be equal to $1/\epsilon$. Therefore the tortuosity factor represents the deviation of a granular mass from this conception of straight parallel pores. The porosity of a granular mass decreases as λ increases. Hence the value of λ/ϵ is a measure of the porosity itself.

Finally there are 10 mercury manometers connected with the filter vessel at a level of 1 cm, 2 cm, 3 cm, etc. above the filter surface. The purpose of these manometers is to measure the pressure distribution in the cake up to pressures of 2 atm.

Photographs of the apparatus are given in Figs. 2 and 3.

3. CONSTANT RATE FILTRATION

In this case the top layer is always formed in the same manner. Therefore the top layer invariably has the same structure and the pressure difference through this layer is also constant. The same applies to a layer at a certain level below the cake surface. Therefore the pressure distribution as a function of the height measured from the top of the cake remains the same during filtration.

This means that in the case of a constant rate filtration the pressure distribution in the cake can be derived from the changes in the total pressure Δp with the cake thickness.

4. RETARDED PACKING COMPRESSIBILITY

During the filtration of slurries of polyvinyl chloride (PVC) fines in water,* a phenomenon was encountered which was shown to be a special kind of packing compressibility. Since at the pressures applied the PVC particles are non-deformable, packing compressibility is the only form of compressibility that can occur. It differs, however, from normal packing compressibility in such a way that it occurs only when filtration has been going on for some time until a critical thickness has been reached. From that moment a layer of denser packing and increasing thickness is formed at the bottom of the cake. The

* Size of PVC. particles : 5-12 μ.

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upper layer the thickness of which remains constant or decreases, retains its original packing and porosity.

This phenomenon was called retarded packing compressibility (r.p.c.). Naturally it greatly affects the average filtration rate.
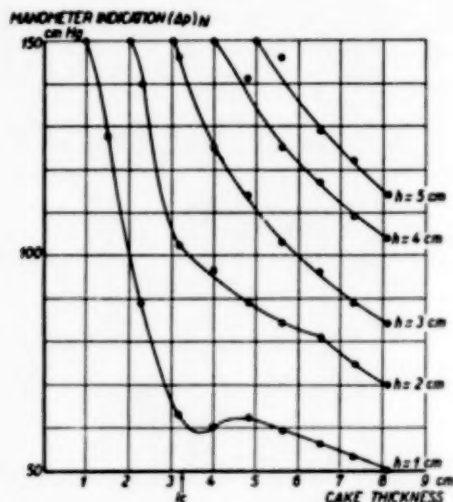

Fig. 4. Pressure distribution through a PVC cake during filtration at a constant pressure of 150 cm Hg (h = height above filter medium).
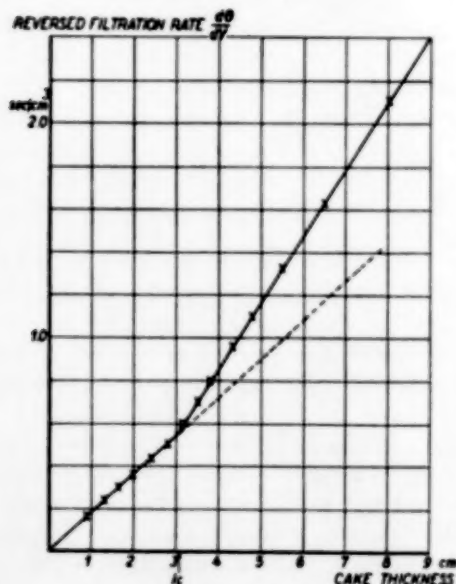

Fig. 5. Course of reversed filtration rate $\frac{d\theta}{dV}$ with cake thickness during filtration of a PVC slurry.

In Fig. 4 graphs of the measured manometer indications are given for varying heights above the filter medium as functions of cake thickness, for the cases in which r.p.c. occurs and the filtration pressure is kept constant at 150 cm Hg.

Fig. 5 shows the course of the reversed filtration rate $d\theta/dV$, which is a measure of the total cake resistance (since in normal cake filtration at a constant pressure the average cake resistance is a constant this curve is a straight line) and, Fig. 6 gives the course of the value of λ/ϵ at different levels as measured with the gauge pins.
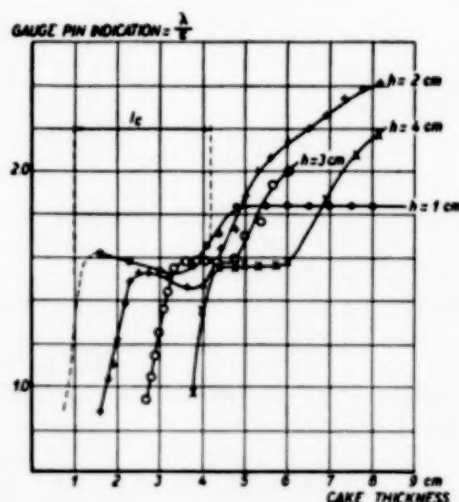

Fig. 6. Course of gauge pin indications during filtration of a PVC slurry (h = height above filter medium).

From these figures it is clear that when the critical cake thickness (indicated by l_c) is reached the pressure difference through the bottom layer increases, the porosity of this layer decreases and the total cake resistance suddenly increases more rapidly than before.

This behaviour can be understood from the above-mentioned hypothesis of a bottom layer of denser packing and increasing thickness after the critical cake thickness is reached.

If we suppose DARCY's equation to hold good for the flow through the cake and we use the conception of the specific cake resistance r instead of the cake permeability we find :

$(\Delta p)_{hl} = \eta v (hr + R)$ where $(\Delta p)_{hl}$ is the pressure difference between the liquid pressures at a height h above the filter cloth and below the cloth, R is the resistance of 1 cm² filter cloth, v the linear velocity, while η stands for the viscosity.

The total filtration pressure difference $\Delta p = \eta v (lr + R)$. Therefore : $(\Delta p)_{hl} = \Delta p \dfrac{hr + R}{lr + R}$

If r.p.c. has occurred and r_1 is the specific resistance of the bottom layer we find :

$$(\Delta p)_{hl} = \Delta p \frac{(l - l_c)\, r_1 + \{h - (l - l_c)\}\, r + R}{(l - l_c)\, r_1 + l_c r + R} \quad \text{for} \quad (1)$$

$$0 < l - l_c < h.$$

$$\text{and } (\Delta p)_{hl} = \Delta p \frac{hr_1 + R}{(l - l_c)\, r_1 + l_c r + R} \quad \text{for } l - l_c > h$$

be explained by this conception. It is easy to derive from DARCY's law that :

$$\frac{d\theta}{dV} = \frac{1}{A} \cdot \frac{\eta\, (lr + R)}{\Delta p} \quad \text{for} \quad l < l_c \qquad (2)$$

and

$$\frac{d\theta}{dV} = \frac{1}{A} \cdot \frac{\eta\, [l_c r + (l - l_c)\, r_1 + R]}{\Delta p} \quad \text{for } l > l_c$$

The gauge pin indications are also in good agreement with this conception of a bottom layer of higher specific resistance.

The phenomenon also occurs in the case of constant rate filtration. Fig. 8 gives the curve for the pressure difference through the whole cake against cake thickness in the case of a filtration rate $dV/d\theta = 15 \cdot 0$
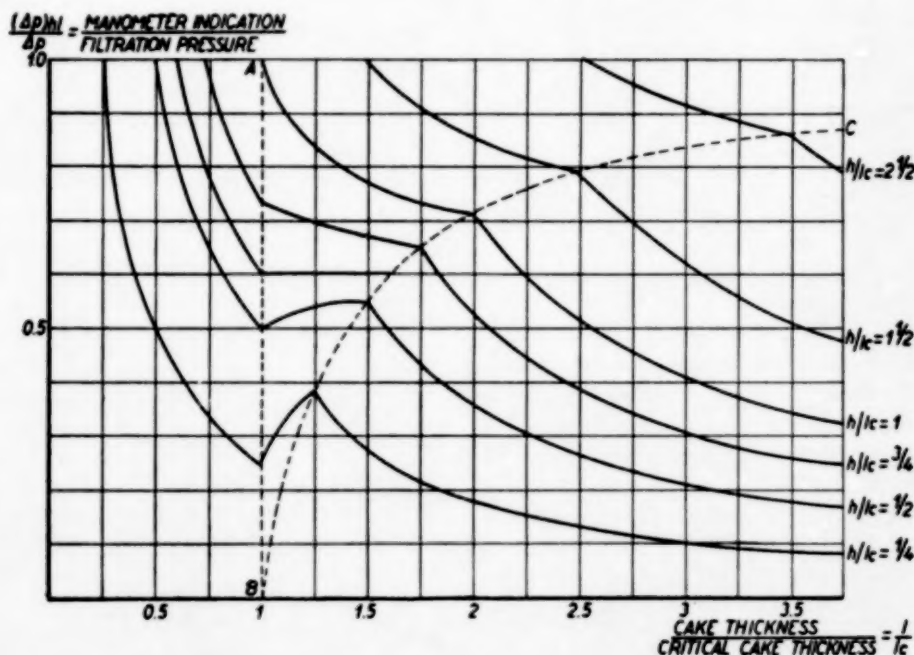

Fig. 7. Theoretical course of manometer indications in the case of r.p.c. ($h =$ height above filter medium) ($r_1/r = 2 \cdot 5$; $R = 0$).

Fig. 7 gives a plot of this theoretical pressure distribution for different values of h and as a function of cake thickness ; the resemblance between Fig. 7 and Fig. 4 is clear.

Also the deflection in the $(d\theta/dV - l)$ curve can

cm³/sec., as well as that of the pressure distribution through the cake as derived from the total pressure. In this case the pressure distribution could not be measured since owing to the constantly increasing pressure the manometer connections were blocked.
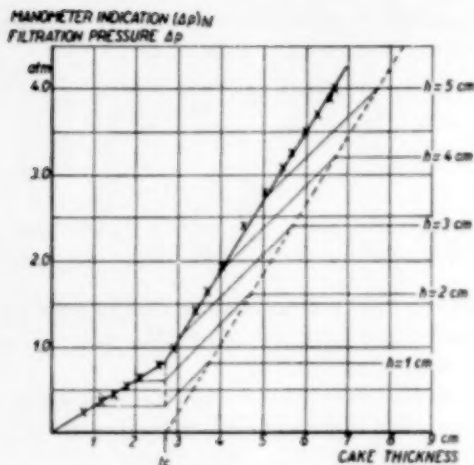
Fig. 8. Course of the filtration pressure in a constant rate filtration (filtration rate $= 1 \cdot 05 \frac{cm^3}{sec}$) of a PVC slurry and derived pressure distribution (h = height above filter medium).

5. POSSIBLE EXPLANATIONS OF r.p.c.

Several explanations have been examined :

(i) the phenomenon is caused by a scouring effect.*

(ii) the cake shows normal compressibility, but this compressibility is slow.

(iii) the lower cake layers are blocked by small air bubbles from the solution.

However, these explanations do not tally with the facts observed. Scoring cannot explain the phenomenon since it would result in a deflection of the $(d\theta/dV - l)$ curve towards the l-axis. Nor did a particle size analysis show smaller particles in the bottom layer.

Slow compressibility can indeed show a more or less pronounced bend, but a mathematical analysis starting from the hypothesis that the specific resistance changes with the time from r_0 to $r_0 (a + 1)$ according to :

$$r = r_0 (a + 1 - a \cdot e^{-\lambda\theta})$$

did not show a sudden increase of the pressure difference across the bottom layer in this case. The third suggestion was contradicted by the constant rate filtration in which case also r.p.c. occurred and

* Scouring is defined as the phenomenon occurring when the very small particles are entrained by the flow through the pores of a cake, which is built up of large particles.

no air was in contact with the slurry in the supply vessel.

Also, when in a constant pressure filtration the slurry in the supply vessel is prevented from coming into contact with the air by means of an oil layer and the slurry is not recirculated, r.p.c. still occurs.

6. STABILIZED CAKE STRUCTURE

A fourth explanation is possible. The sudden character of the phenomenon points to a stabilizing effect of the original cake structure. If this effect should originate from the liquid flow through the cake and therefore be proportional to the filtration rate (or to a power of the filtration rate), it may occur that as the filtration is going on and the filtration rate decreases, this stabilizing effect becomes too small and then the cake is compressed first at the bottom where the cake pressure has its highest value, and later also higher in the cake.

The fact that no r.p.c. occurs when the filter is vibrated at sound frequencies and that in that case the filtration rate decreases according to the steeper part of the $(d\theta/dV - l)$ curve, also points to a stabilized structure when the filter is not vibrated.

It will now be described how a stabilizing effect can occur :

When a random packing of rather loose structure is compressed, it is necessary that each particle should move not only in a vertical but also in a horizontal direction (supposing the compressing force to act in a vertical direction). If the non-deformable particles could move only in a vertical direction, compression of the packing would not be possible (see Fig. 9).
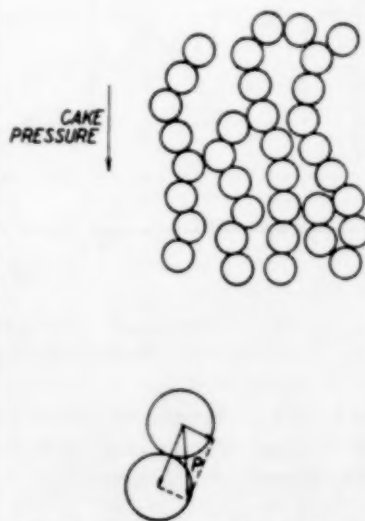
The compressing force originates from the cake pressure already mentioned, which increases from top

Fig. 9. Picture of a cake structure.
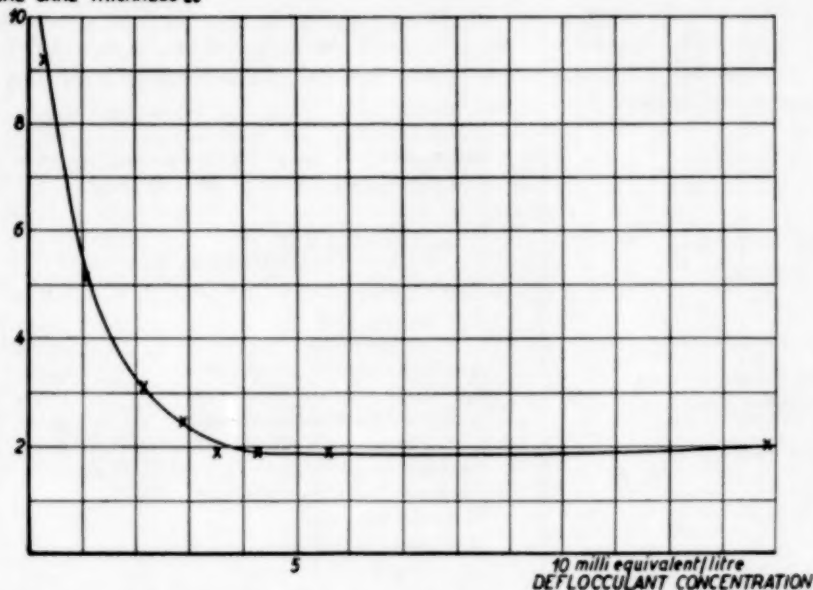
CRITICAL CAKE THICKNESS t

10 milli equivalent/litre
DEFLOCCULANT CONCENTRATION

Fig. 10.   Course of critical cake thickness with deflocculant concentration in filtration of PVC slurries at a constant pressure of 150 cm Hg.

Whether or not the packing is stabilized therefore depends on the height in the cake and also on the total cake thickness. As long as the critical cake thickness has not been reached the whole cake is stabilized. Afterwards only the upper part is stabilized, while the lower compressed part steadily increases in thickness.

It was noticed that ions present in the slurry liquid have a strong influence on the critical cake thickness. In Fig. 10 the influence of the deflocculant concentration on the critical cake thickness is shown. The deflocculant was sodium dodecyl sulphate, the slurry liquid ordinary tap water. In Fig. 11 the influence of the concentration of sodium chloride and calcium chloride on the critical cake thickness is plotted. In these cases distilled water was used for the slurry liquid and some deflocculant (4 millimols/litre) was added.
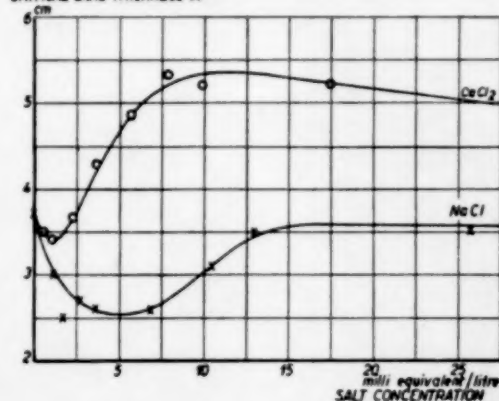
to bottom. If the component of this compressing force which tries to move the particle in a direction other than the vertical, is counterbalanced by a second force of other origin, compression will be prevented ; the cake structure is stabilized and will retain its packing density and porosity.

As already suggested, such a stabilizing force should be the same throughout the cake and should originate from the liquid flow. Therefore the stabilizing force should decrease when the filtration rate decreases.

Summarizing, we have, according to our theory :
(1) A compressing force, which increases from top to bottom of the cake
(2) A stabilizing force originating from the liquid flow and decreasing as the filtration rate decreases or the cake thickness increases.
(3) When the stabilizing force is equal to or larger than the component of the compressing force which tries to displace the particle in a horizontal direction, this displacement is prevented and the packing retains its structure and porosity.
(4) When the stabilizing force is smaller, the packing is rearranged and the porosity is lowered.

CRITICAL CAKE THICKNESS t

CaCl₂

NaCl

20
milli equivalent/litre
SALT CONCENTRATION

Fig. 11.   Course of critical cake thickness with salt concentrations (salt being CaCl₂ and NaCl resp.) in filtration of PVC slurries at a constant pressure of 150 cm Hg.

At low concentrations Na-ions and Ca-ions have similar effects; the influence of Ca-ions, however, is much stronger. At higher concentrations Ca-ions have a different effect, probably caused by a certain de-activation of the deflocculant by these ions.
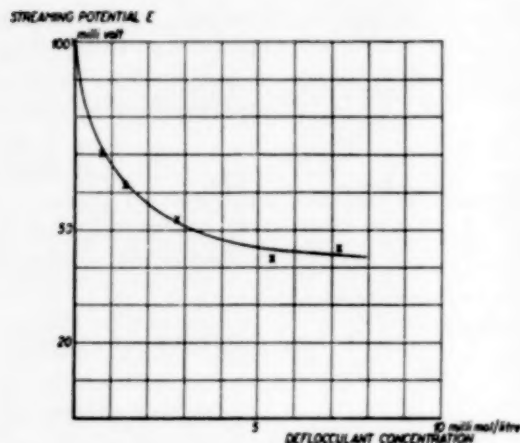

Fig. 12. Course of streaming potential with deflocculant concentration in filtration of PVC slurries at a constant pressure of 150 cm Hg.

The strong influence of ions present in the slurry as well as the necessary relation between the stabilizing force and the filtration rate points to an electrokinetic nature of this stabilizing force.

However, how such a stabilizing force should originate from electrokinetic phenomena is not quite clear. Efforts to correlate the critical cake thickness

with the streaming potential across a filter cake (in an all-glass apparatus) have so far been unsuccessful.

It is beyond the scope of this article to discuss these results in detail. They will be published elsewhere*.

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* K. RIETEMA : *A study on the compressibility of filter cakes.* Thesis, Technological University of Delft, 1952.

NOTATION

		Dimensions
P	= cake pressure	$gr.cm^{-1}sec.^{-2}$
p_d	= particle pressure	$gr.cm^{-1}sec.^{-2}$
p_l	= liquid pressure in the cake	$gr.cm^{-1}sec.^{-2}$
p_0	= liquid pressure over the cake	$gr.cm^{-1}sec.^{-2}$
Δp	= filtration pressure difference	$gr.cm^{-1}sec.^{-2}$
$(\Delta p)_{hl}$	= difference in liquid pressure at a height h in the cake with thickness l and the liquid pressure below the filter cloth	$gr.cm^{-1}sec.^{-2}$
l	= cake thickness	cm
h	= height in the cake	cm
l_c	= critical cake thickness	cm
ϵ	= porosity = $\dfrac{\text{volume of voids}}{\text{volume of cake}}$	
λ	= tortuosity factor	
v	= linear velocity	$cm.sec.^{-1}$
V	= volume of filtrate	cm^3
θ	= time of filtration	sec.
η	= viscosity	$gr.cm^{-1}sec.^{-1}$
r	= specific resistance	cm^{-2}
r_1	= specific resistance of lower compressed layer	cm^{-2}
R	= resistance of 1 cm² filter cloth	cm^{-1}
A	= filter surface area	cm^2
E	= streaming potential	$gr.^{\frac{1}{2}}cm^{\frac{1}{2}}sec^{-1}$
D	= dielectric constant of filtrate	
d	= average particle diameter	cm

Book reviews

G. KORTÜM and H. BUCHHOLZ-MEISENHEIMER : **Die Theorie der Destillation und Extraktion von Flüssigkeiten.** 381 pp. Springer Verlag Berlin, Göttingen, Heidelberg, 1952. DM. 39.60 or £3 9s. 4d.

PROF. DR. G. KORTÜM, author of some earlier works on electrochemistry (*Elektrolytlösungen*, 1941, and *Lehrbuch der Elektrochemie*, 1947), has now published the above-mentioned book, in collaboration with Dr. H. BUCHHOLZ-MEISENHEIMER. As will appear afterwards, this book also deals with *Lösungen*, but not especially with solutions of electrolytes. The fact that the authors did not entitle their book " Die Theorie der Destillation und Extraktion," but *Die Theorie der Destillation und Extraktion von Flüssigkeiten*, makes us at once presume that they do not give a treatise on distillation and extraction as unit operations but are especially concerned with the mixtures which are subjected to distillation or extraction. The authors consider the liquid mixtures (eventually in the presence of a vapour or a second liquid phase) from the thermodynamic point of view. Many years ago the theory of such mixtures was already developed by the Dutch school (VAN DER WAALS, SCHREINEMAKERS, KUENEN VAN LAAR and others). The authors have now undertaken to present this theory in an easily surveyable form, taking into account the results of statistical and molecular considerations and the strongly increased amount of experimental material.

The new edition of HILDEBRAND and SCOTT's *Solubility of Non-electrolytes* is the pendant of the work under review. The book by HILDEBRAND and SCOTT has the character of a review of what has been attained during the last decades in the theoretical and experimental fields with respect to liquid mixtures. A characteristic feature is the statistical approach to the matter. In the work by KORTÜM and BUCHHOLZ-MEISENHEIMER the results of the more recent investigations are skilfully taken into account, but the stress is laid on what may be said from the thermodynamic point of view about mixtures of liquids (whether or not in the presence of a vapour or a second liquid phase).

The first two chapters are of a purely thermodynamic nature ; stability conditions and coexistence equations are derived and conclusions drawn from them. In the third chapter the practical classification of liquid mixtures into ideal, athermic, regular and irregular mixtures is discussed. The fourth chapter is devoted to the series developments of activity coefficients and their application. In Chapters 5 and 6 the liquid-liquid and vapour-liquid equilibria of binary and ternary systems are treated in the light of the preceding chapters by means of numerous state diagrams. Finally, the seventh chapter deals with the separation of liquid mixtures by normal rectification, azeotropic rectification, extractive rectification and by extraction. A good explanation is given of the course of distillation and rectification curves for ternary systems ; the remarkable phenomenon of the temporary fall of the top temperature in the rectification of some mixtures, e.g. of a mixture of methanol, acetone and chloroform, is explained. In the paragraph about extractive rectification mention might have been made of a useful equation for the mean logarithm of the relative volatility given by HERINGTON (1950). At the end of the book there is an extensive author index and a subject index.

The authors have succeeded in treating their subject-matter very lucidly. The reader is supposed to have an average knowledge of thermodynamics. The book is of great theoretical and practical importance to anyone concerned with problems in the fields of distillation and extraction, in so far as they relate to liquid-liquid and liquid-vapour equilibria, state quantities and the selection of substances.

J. BUITEN.

CARL ZERBE : **Mineralöle und verwandte Produkte, Ein Handbuch für das Laboratorium.** Springer-Verlag, Berlin, Göttingen, Heidelberg, 1952. 1525 pp., DM 192 or £16 16s.

This book takes the place of the well-known and highly appreciated work by D. HOLDE, *Kohlenwasserstofföle und Fette*, the last edition of which appeared about twenty years ago.

It is readily understood that after the revolutionary development of the research of hydrocarbon mixtures and, to a certain extent, of the fatty oils, it was no easy task to prepare a new edition of this work.

We may thank the author for shouldering these enormous responsibilities, for which he secured the collaboration of many colleagues, specialists in various fields.

Chapters I, II, III and IV, in that order, deal with : General Methods of Investigation, Mineral Oils and their Products, Motor Fuels, including the gaseous fuels, and Lubricants. They cover no less than 1029 pages, which is over two-thirds of the whole book.

In chapter V more than 140 pages are devoted to the discussion of tar and tar products. Attention has been given to the standardized specifications, including the American and British standards. Following those mentioned above there are several shorter chapters. It may be useful to state here that chapter IX is devoted to the vegetable and animals oils and fats (86 pp.) and chapter X to resins, turpentine oil and some waxes.

From the foregoing it will be clear that the emphasis is laid on mineral oil research ; the fatty oils are only treated in so far as this was necessary for the constitution of a transition.

It should furthermore be mentioned that the author has tried to keep in contact with the relative production methods. This is evident from the chapter on Catalytic Hydrogenation under Pressure (VI) and that on the Fischer-Tropsch Synthesis (VII).

The last chapter (XI) deals with bleaching earths (6 pp.). The index covers over ninety pages.

In the long list of collaborators we find the names of many well-known investigators such as Prof. Dr. G. R. Schultze (Hannover), Dr. H. Kölbel (Hamburg) and Dr. W. Krönig, to mention only a few.

It it obvious that a work such as Zerbe's, which has to deal with such an enormous amount of material, cannot be complete. This provides a point of criticism. However, the book satisfies reasonable demands, for which reason the reviewer is convinced that it will find its way into every laboratory for mineral oil research, and related products.

H. I. WATERMAN.